

Carbon microtubes: tuning internal diameters and conical angles

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Abstract

In this paper, we report a synthesis strategy for a new class of hollow, curved carbon morphologies, ‘carbon microtubes’ (CMTs), with absolute control over their conical angles and internal diameters. Our synthesis methodology employs nitrogen or oxygen dosing to change the wetting behaviour of gallium metal with the growing carbon walls to tune the conical angles. Increasing N₂ concentrations in the gas phase during growth increases the conical angles of CMTs from +25° to about –20°. A methodology using the timing of oxygen or nitrogen dosing during CMT growth is shown to tune the internal diameters anywhere from a few nanometres to a few microns. The walls of the carbon microtubes are characterized using transmission electron microscopy (TEM) and Raman spectroscopy and are found to consist of aligned graphite nanocrystals (2–5 nm in size). Furthermore, dark field images of CMTs showed that the graphite nanocrystals are aligned with their *c*-axes perpendicular to the wall surface and that the crystals themselves are oriented with respect to the wall surface depending upon the conical angle of the CMT.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The unique electrical, chemical and mechanical properties of carbon nanotubes (CNTs) offer enormous potential for a wide range of applications. However, the potential of carbon nanotubes (CNTs) for microfluidics applications is limited owing to their smaller inner diameters (typically 1–10 nm). In addition, CNTs often have bamboo styled internal obstructions as a result of their typical growth process [1, 2]. The smaller inner diameters and internal obstructions pose challenges to fluid flow applications. Carbon tubes with larger inner diameters are ideal candidates for microfluidic applications such as micro-pumps, flow channels and nano/micro reactors.

Libera and Gogotsi [3, 4] used a hydrothermal technique to synthesize carbon tubular structures with diameters ranging from 70 to 1300 nm with fluid (water) encapsulated between

internal obstructions. Gao and co-workers synthesized gallium filled carbon nanotubes using carbothermal reduction using gallium oxide and activated carbon [5, 6]. These gallium filled carbon nanotubes have been projected as carbon nanothermometers based on the movement of gallium within the tube as a response to temperature variations. However, the resulting carbon tubular structures were straight and the internal diameters were limited to sizes much below a micron. Hu *et al* [7] recently reported the synthesis of carbon tubes with diameters in the range of 1–2 μm using a technique similar to carbothermal reduction but with ZnS powder. Earlier, we reported a concept employing low-melting metals such as Ga to synthesize a wide variety of carbon tubular morphologies (cones, tubes, funnels, n-staged structures and Y-junctions) [8] with large internal diameters referred to here as carbon microtubes (CMTs). Using low melting metals to mediate carbon film growth on their surface allows us to tune the morphology of the carbon shell or wall around the droplet by appropriately varying the shape of the liquid during growth.

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In other words, it can be visualized as a process where the shape of the catalyst particle is changed constantly during growth. However, it must be emphasized here that gallium is not catalytic to carbon tube growth. Rather, molybdenum (Mo) was used to promote carbon deposition onto Ga.

In this paper, we have extended the above concept for absolute control over the internal diameters and the conical angles of the resulting carbon microtubular structures. The wall structures are critically examined using transmission electron microscopy to provide insight into the microscopic growth mechanism involved. In order to generalize the synthesis concept, studies were also performed using indium instead of gallium. In the rest of the discussion, carbon microtubes (CMTs) are used to refer to various morphologies, not just straight tubes.

2. Experimental details

The synthesis experiments were performed in a Microwave Plasma CVD chamber operated at 600–1100 W and 40–90 Torr reactor pressure. A thin film of gallium spread onto a graphite substrate followed by molybdenum powder dusting was exposed to 18% CH₄/H₂ plasma. In order to tune the conical angles and internal diameters, different N₂/O₂ dosages were used at various stages of growth. The appropriate dosing amounts as well as the timing of the impurity addition will be discussed in detail.

The wall structure of CMTs thus synthesized was analysed using selected area diffraction (SAD), electron nanodiffraction (END), dark field scanning transmission electron microscope (STEM) imaging and Raman spectroscopy.

3. Results and discussion

3.1. Macroscopic growth mechanism

Gallium is a low melting metal with extremely low vapour pressures over a range of temperatures (30–1200 °C). The solubility of carbon in gallium is expected to be very low and is in fact unknown. Also, gallium is not known to form any carbide under the conditions used here. Ga is also not known to catalyze carbon deposition from a hydrocarbon gas phase, so molybdenum is used here to promote the precipitation of carbon onto the gallium droplets. Upon exposure to plasma, the gallium film on the substrate splits into several droplets. The growth mechanism for carbon tube formation around the liquid metal droplets is illustrated in figure 1. The growth of tubes is initiated with the deposited carbon forming a wall or a sheet around the droplet. Further addition of carbon lifts the gallium droplet by continuing the growth at the gallium–carbon interface as shown in figure 1(b). Macroscopically, the morphology of the evolving structure depends on the curvature of the gallium droplet, or the contact angle, at the gallium–carbon interface. Based on the schematic shown in figure 1, the conical angle of the evolving morphology can be related to the contact angle by the relation

$$\phi = 2\theta - 180^\circ. \quad (1)$$

Our hypothesis for the above growth concept is that the conical angle can be altered *in situ* during growth by changing

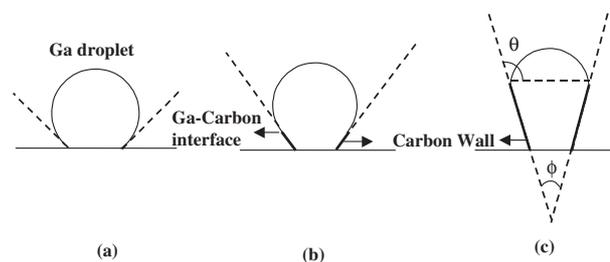


Figure 1. Schematic illustrating the macroscopic growth mechanism involved for carbon micro-tubular growth using low-melting metals: (a) formation of the initial Ga droplets upon plasma exposure; (b) formation of carbon shell around the Ga droplet and further addition of carbon at the Ga–C interface; and (c) the geometric definition of the contact angle and conical angle of CMTs.

the contact angle, θ . Under normal conditions, gallium does not wet carbon due to its high surface tension. However, gallium can be made to wet carbon, in the presence of activated oxygen and nitrogen, which reduces the contact angle θ [9–11].

3.2. Tuning the conical angles

Earlier experiments showed how one could use oxygen to synthesize various morphologies such as straight tubes, tube-on-cone, cone-on-tube (funnel) and other multistaged morphologies [8]. In those experiments, 5 sccm of oxygen was added and removed at different stages of growth to ‘tune’ the morphology *in situ* during growth. Even such a low amount of oxygen is sufficient to reduce the contact angle and form straight tubes (conical angle 0°). The further reduction in contact angles to result in negative conical angles requires the use of much higher oxygen dosages. However, higher oxygen concentrations lead to the spontaneous formation of gallium oxide nanostructures [9]. Nitrogen, on the other hand, has the same qualitative effect as oxygen but does not form gallium nitride under the conditions used here. The nitrogen dissolution necessary for GaN formation requires increased temperatures and high amounts of dissociated nitrogen [11]. Therefore, the amount of nitrogen added to the feed gas composition can be used as an ideal ‘tuner’ to obtain CMTs with conical angles over a wide range.

The conical angles of CMTs obtained without the presence of O₂ or N₂ are typically around 20–25°. The addition of nitrogen to the feed gases throughout the duration of growth reduces the contact angle between carbon and gallium, thus reducing the conical angles of CMTs. For example, the addition of 10 sccm of nitrogen (in 18 sccm CH₄/100 sccm H₂ feed gases) reduced the average conical angles to 0°–5°. Increased nitrogen dosing further reduced the conical angles, yielding CMTs with ‘negative’ conical angles. Here, the negative conical angles refer to CMTs whose diameters decrease during growth along the conical axis (in other words, converging cones). Control over the conical angles of CMTs is easily obtained using different amounts of N₂ (10–35 sccm) as illustrated in figure 2. The normalized distribution of conical angles is also shown in figure 2. Note that the conical angles decrease as the N₂ concentration increases, and intermediate N₂ dosages yield straight tubes with zero or very low conical angles.

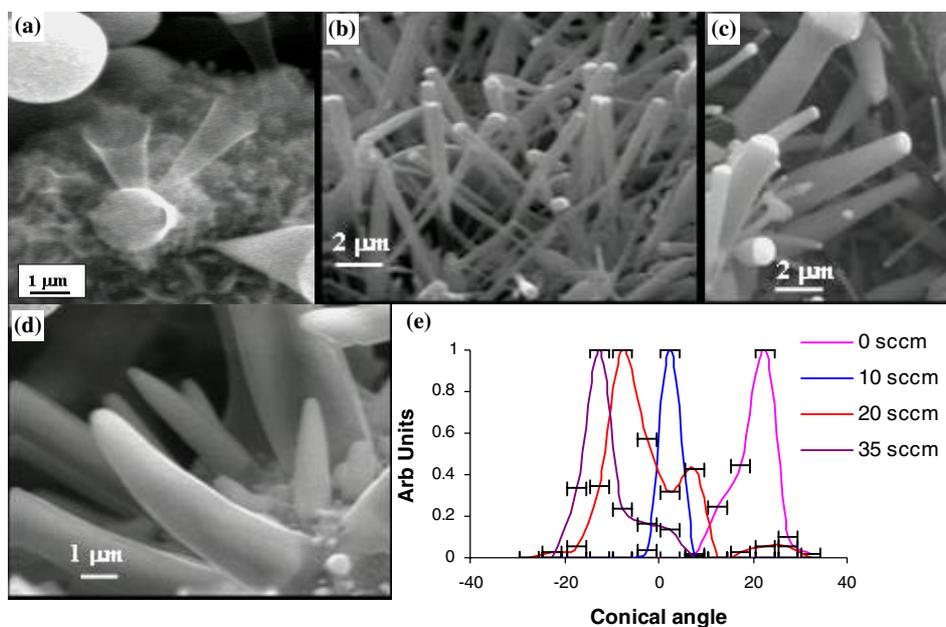


Figure 2. Tuning the conical angles of carbon microtubes. (a)–(d) SEM micrographs of conical morphologies obtained by using increased N₂ dosing in the feed gases: (a) 0 sccm, (b) 10 sccm, (c) 20 sccm and (d) 35 sccm. (e) Normalized distribution of conical angles obtained from samples shown in (a)–(d).

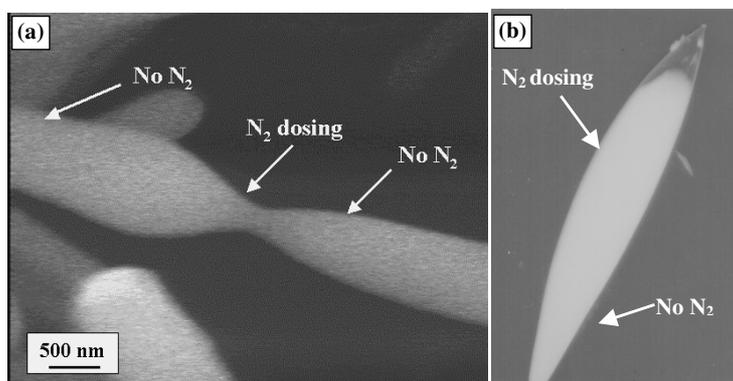


Figure 3. (a) SEM micrograph of the dumbbell morphology obtained using a three-step sequence involving a 'no-nitrogen–nitrogen–no-nitrogen' dosing sequence during growth. (b) TEM micrograph of the capsule morphology obtained using a two-step sequence involving a 'no-nitrogen–nitrogen' dosing sequence.

3.3. Dumbbell and capsule morphologies

Using high nitrogen concentrations to create negative conical angles resulted in new morphologies such as dumbbells and capsules as shown in figure 3. For example, a three-step dosing sequence resulted in the 'dumbbell' morphology. The first stage of growth using no O₂ or N₂ dosing led to diverging conical growth. The second stage of growth using high N₂ dosing resulted in a converging cone. The third stage of the growth using no nitrogen dosing caused the growth to lead to a diverging cone again. By appropriately choosing the N₂ dosing amount, i.e. the flow rate and duration of N₂ dosing, one can tune the diameter of the 'pinched region' and also use this factor to close one end of the tube, creating a capsule morphology. Capsule morphologies result from a two-step dosing sequence. The first stage of the growth involves no nitrogen dosing, and the second stage requires a high amount of N₂ dosing. The high N₂ flow rate during the second stage causes the diameter

to continuously decrease, eventually closing the growing end of the tube. Thus, a 'capsule' morphology with one end open and one end closed was synthesized.

3.4. Tuning the internal diameters

A simple methodology using a two-step sequence consisting of no oxygen dosing followed by oxygen dosing (5 sccm) during CMT growth is illustrated here. As illustrated earlier, the first part of the growth is expected to yield diverging conical growth with increasing diameter along the axis of the cone. In the second part of the growth, after oxygen dosing, a straight tube is expected. So, the diameter of the resulting tube can be tuned by appropriately timing the oxygen dosing during CMT growth as illustrated in figure 4. Experiments performed with oxygen dosing in the first 10 min of the experiment (1 h total) resulted in straight tubes with diameters ≈ 150 nm. Later experiments with oxygen dosing after 20 and 30 min of initial

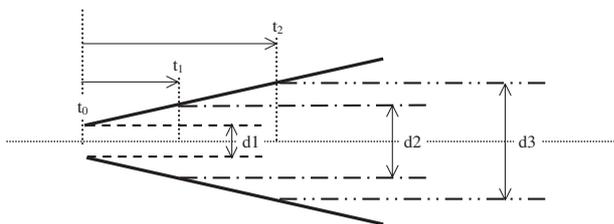


Figure 4. A schematic representation of the strategy used for tuning the internal diameters of CMTs. The strategy, as indicated by dashed lines, involves timing, t , of the oxygen or nitrogen dosing appropriately for obtaining final diameter, d , of the CMT.

conical CMT growth resulted in straight tubes with diameters ≈ 600 and 1800 nm, respectively. The diameter distribution and the associated SEM micrographs are shown in figure 5.

The diameters possible with such a strategy are only limited by the amount of gallium, which in our experiments is limited due to the usage of Ga thin film. However, it is possible to increase the diameters further by using a gas phase source of gallium such as tri-methyl gallium. For example, some of our experiments also yielded a few microtubes with internal diameters as large as $15 \mu\text{m}$, as shown in figure 6. However, the occurrence of such tubes is very sparse due to a combination of factors: limited supply of gallium, distribution of gallium droplet sizes upon plasma exposure and re-coalescence of gallium droplets during growth. Nevertheless, based on the above observation, it can be concluded that carbon microtubes with much larger diameters can be synthesized using our technique.

3.5. Wall structure

The conical angles of CMTs obtained using our technique do not match the conical angles expected when the cones were obtained by perfect folding of graphene sheets using standard arrangements of carbon atoms [12]. There are only five standard conical angles that can be geometrically expected with a single graphene sheet containing a five-, six- or sevenfold arrangement of carbon atoms [13]. In the case of other conical structures, such as carbon nanopipettes [14] and graphite whiskers [15], the wall can still be represented as continuously scrolled graphene sheets to form a conical structure with the edge sites exposed along the outer surface. In the case of CNTs (either multi-walled or single walled), the wall can be visualized as concentric cylinders made up of graphene sheets or a graphene sheet rolled into a cylinder. In our case, the CMTs are multi-walled in nature and have both ends open. In addition, due to continuously varying diameters along the conical axis during growth, the wall structure should be different from regular carbon cones or CNTs.

The wall structure of CMTs was investigated using several electron microscopy techniques such as selected area diffraction (SAD), electron nanodiffraction (END) and dark field STEM imaging. SAD was used to determine the crystallinity of CMTs over a large area. A typical SAD pattern taken from the tubes is shown in figure 7. In this case, the tube is bent and the SAD pattern shows two pairs of (002) reflections. Dark field images obtained using these two pairs of (002) reflections indicated that these reflections result from two different regions of the tube that are formed at the bent part of the tube. As can be seen from the SAD

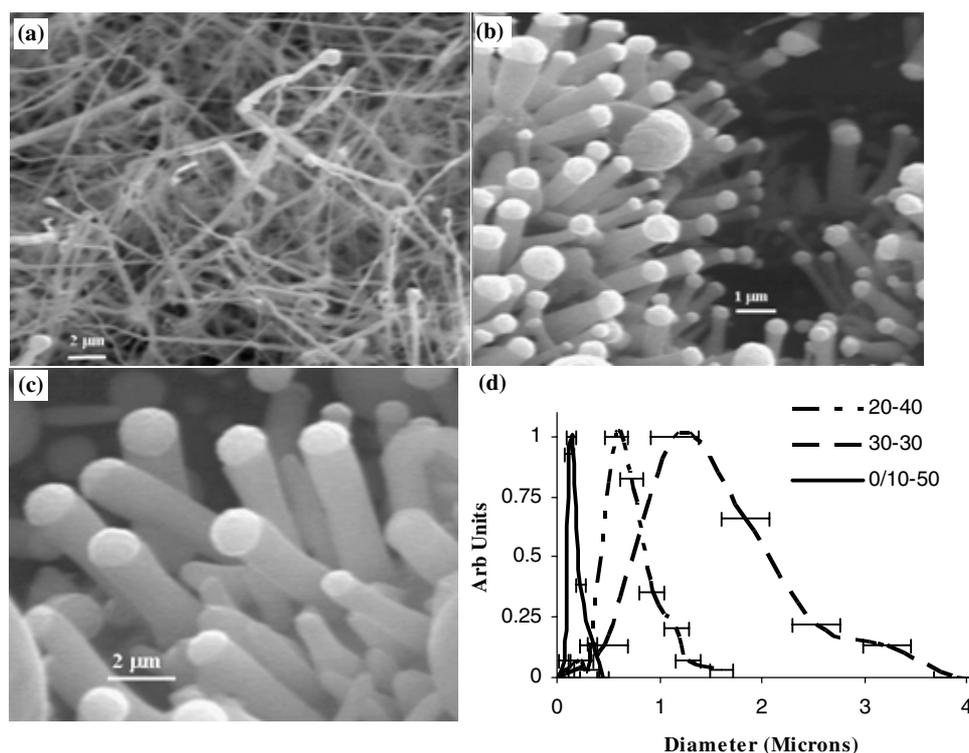


Figure 5. Tuning internal diameters of carbon microtubes. SEM micrographs of CMTs synthesized by oxygen dosing (a) 0–10 min, (b) 20 min and (c) 30 min after the start of the experiment. (d) Normalized distribution of diameters obtained from samples shown in (a)–(c).

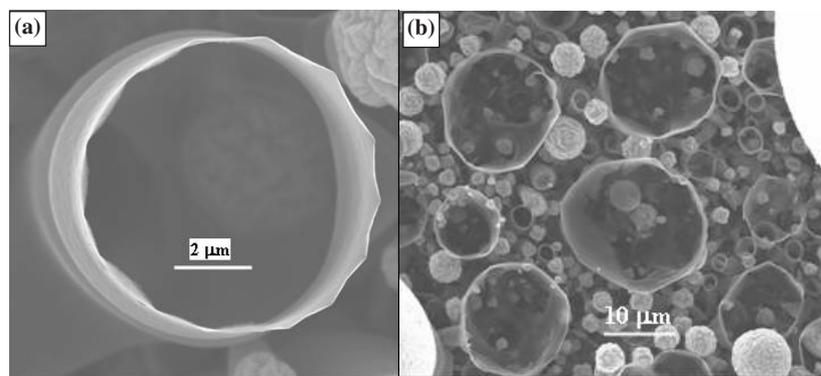


Figure 6. SEM micrographs of carbon microtubes with larger internal diameters in the range of 10–15 μm .

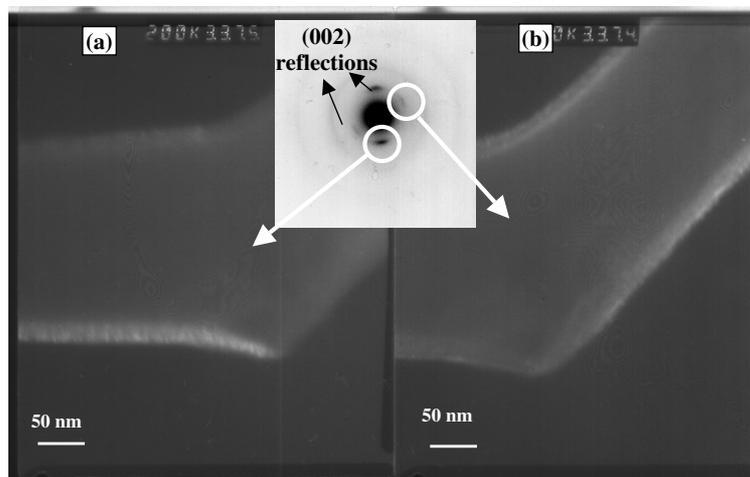


Figure 7. ((a), (b)): Dark field TEM micrographs of CMTs using two pairs of (002) reflections. The inset shows the selected area electron diffraction taken from the bent tube.

pattern, (002) spots are more prominent, whereas (100) and (110) reflections are very weak and diffuse. This is indicative of a lack of long-range order in the wall. In all the tubes studied using SAD, the (002) reflections were found to be always perpendicular to the wall surface, indicating that the *c*-planes of graphite are parallel to the wall surface, but not to the tube axis, except for the straight tubes. Although SAD revealed the crystalline nature of the wall, the detailed wall structure could not be determined. Electron nanodiffraction was used to study the wall structure in detail. In this technique, diffraction patterns from extremely small specimen areas can be obtained by using an incident electron beam with a diameter less than 1 nm. In the case of CMTs, the wall thickness is in the range of 10–20 nm. Therefore, nanodiffraction was used to locally probe the wall structure. Refer to a recent review by Cowley [16] regarding the details of the electron nanodiffraction technique and its applications. The electron nanodiffraction patterns showed strong (002) reflections and very weak (100) and (110) reflections. Dark field STEM imaging using the (002) reflections showed that the wall is comprised of graphite nanocrystals that are about 2–5 nm in size as illustrated in figure 8. The bright regions in the dark field images correspond to nanocrystals of graphite.

These graphite nanocrystals were observed to occur in a set of parallel lines separated by about 5–6 nm, with a specific orientation with respect to the wall surface. This orientation

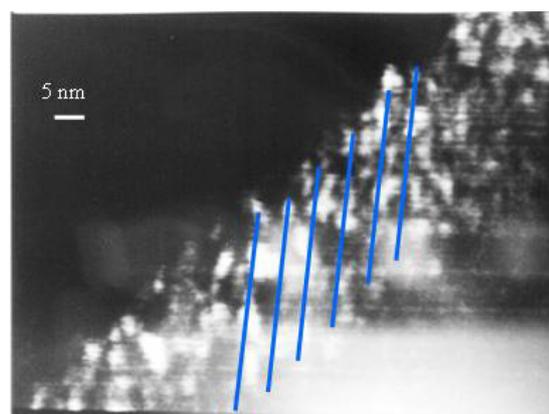


Figure 8. Dark field STEM image of the carbon wall using (002) reflection.

between the parallel set of graphite nanocrystals and the wall surface varied from one tube to another depending on the conical angle of the tube. The orientation of these parallel lines of graphite nanocrystals with the wall surface is similar to the angle that gallium makes with the wall within about 10° , as shown in figure 9. This can be attributed to changes in the contact angle due to temperature variations between the growth and the TEM analysis. In other words, the wall consists

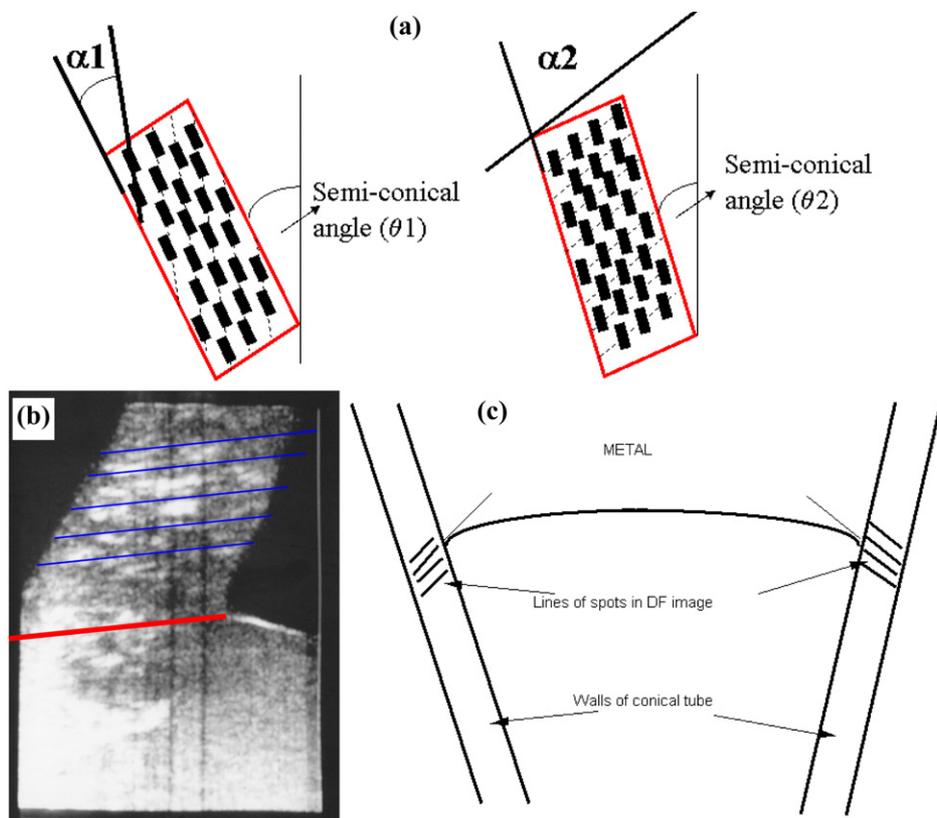


Figure 9. (a) Schematic representation showing the difference in orientation of the parallel set of graphite nanocrystals with the carbon wall (α_1, α_2) in two CMTs with two different conical angles ($2\theta_1$ and $2\theta_2$), (b) dark field image of the wall of a CMT at the gallium-carbon interface region and (c) schematic illustration of the orientation of the parallel set of graphite nanocrystals with the wall surface. The orientation is very close to the angle that the gallium makes with the wall surface.

of nanocrystals of graphite that have similar orientations with respect to the wall surface just as the orientation of liquid gallium inside the tube to the carbon wall.

As the beam was moved nearly perpendicular to the lines of spots in the dark-field images, the diffraction pattern almost always consisted of the (002) lines of spots with varying intensities and vague indications of (100) and (110) reflections. By translating the beam just a few nanometres, the diffraction pattern changed from having both orders of (002) reflections strong to having one order strong and other order almost zero. Sometimes, the diffraction spots are not symmetrical about the origin, and in some cases the first order reflection intensities were very different. This can only happen when the crystal is thick, suggesting that the crystal is elongated along the beam direction. For thin crystals (less than 1 nm thick), where the scattering is kinematical, the two spots should have equal intensities. For one spot to be very much stronger than the other there must be strong dynamical scattering and the thickness must be of the order of an ‘extinction distance’. In the case of graphite this is about 20 nm or more. This suggests that the graphite crystals are elongated along the direction tangential to the wall surface as shown schematically in figure 10.

The wall structure of CMTs was further investigated using Raman spectroscopy. Raman spectra taken from CMTs using two different laser wavelengths (633 and 325 nm) are shown in figure 11. The presence of two peaks at around 1350 and 1580 cm^{-1} is indicative of the D and G bands of graphite, respectively [17]. The position and intensity of the D band are

dependent on the crystal size and the laser wavelength. The D band shifts to higher wavenumbers with decreasing laser wavelengths. The observed shift in the D band by decreasing the laser wavelength from 633 nm (1.9 eV) to 325 nm (3.8 eV) is consistent with the expected shift of 50 $\text{cm}^{-1} \text{eV}^{-1}$ [18, 19], with no appreciable shift in the G band, as shown in figure 11. Using the relative intensities of the D and G bands, the cluster size of the graphite crystals was calculated using Knight’s formula:

$$L_a = C(I_G/I_D) \quad (2)$$

where L_a is the cluster size, I_G and I_D are the G and D band intensities, respectively, and C is a constant dependent on the laser wavelength. Using a value of 8.3 nm [19] for C at a wavelength of 633 nm, the cluster size of graphite in CMTs was determined to be 7 nm, consistent with the TEM investigations described earlier.

3.6. Microscopic growth mechanism

Based on the wall structure, a microscopic growth mechanism for the formation of a carbon wall with nanocrystals of graphite is proposed. In the case of the CMT growth described here, the addition of carbon to the growing end of the tube seems to occur either directly from the gas phase or from the surface diffusion of adsorbed carbonaceous species on the gallium droplet. Since the diameter of the gallium on which carbon addition occurs is larger, the graphene sheet that forms around

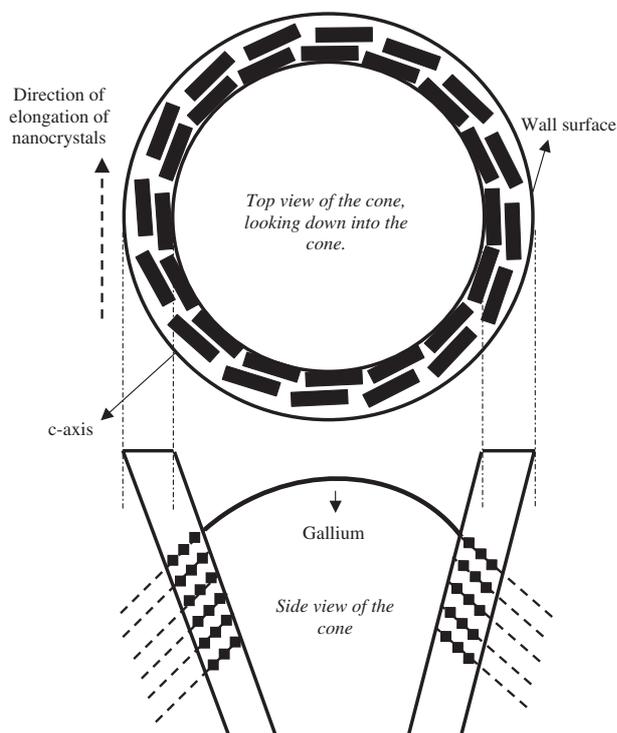


Figure 10. Schematic illustration of the wall structure. The elongation of graphite nanocrystals along the direction tangential to the wall surface is indicated by a dashed arrow in the top view and the preferential alignment of graphite nanocrystals with respect to the wall surface is shown in the side view.

the droplet breaks up to accommodate the stress, thus creating nanocrystals of graphite that are longer along the direction tangential to the wall surface. The breaking up of graphene sheets into nanocrystals is not surprising. It has been observed in multi-walled CNTs that graphene sheets slide over one another to accommodate the misfit caused by increase in diameters with the addition of subsequent graphene layers [20]. TEM investigations performed along a certain length at the tip of the microtubes revealed that the wall tapers down to a few layers of graphene as shown in figure 12. This is further indicative that the wall is always tangential to the gallium surface and that the contact angle between gallium and carbon is always maintained. This information also indicates that the carbon addition occurs right at the tip. Since a constant wall thickness is maintained for the rest of the length, it is expected that the carbon atoms that are added at the tip diffuse downwards in a spiral fashion, causing elongation of crystals along the tangential direction as shown in figure 12(b).

The growth concept proposed here and the strategies suggested for tuning the conical angles, morphologies and internal diameters can be generically applied not just to carbon–gallium systems but also to other systems. For example, CMTs were also synthesized by replacing gallium with indium, another low melting metal with a low solubility for carbon (not shown here). The ‘straight’ tube morphology observed in the studies by Gao *et al* [5, 6] and Hu *et al* [7] could easily be explained using our arguments that the presence of species such as oxygen, nitrogen and/or sulfur could lower the contact angle between low-melting metals and carbon and promote the growth of straighter tubes.

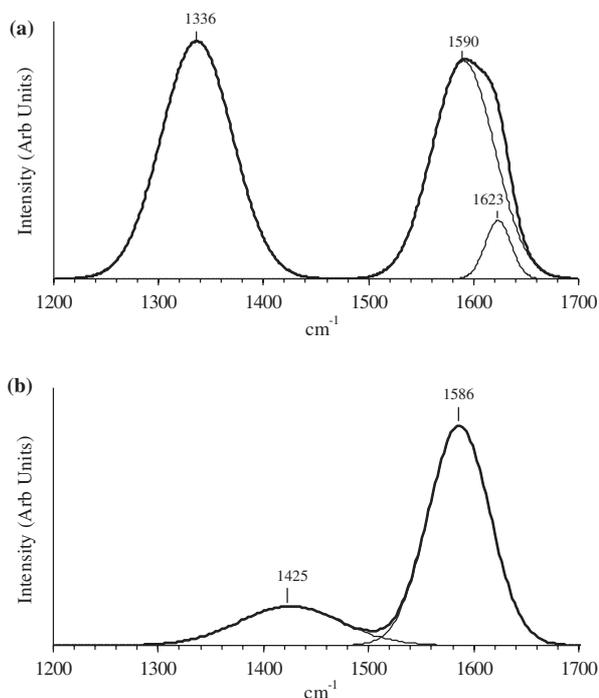


Figure 11. Raman spectra of carbon microtubes obtained using (a) 633 nm and (b) 325 nm wavelength laser excitation.

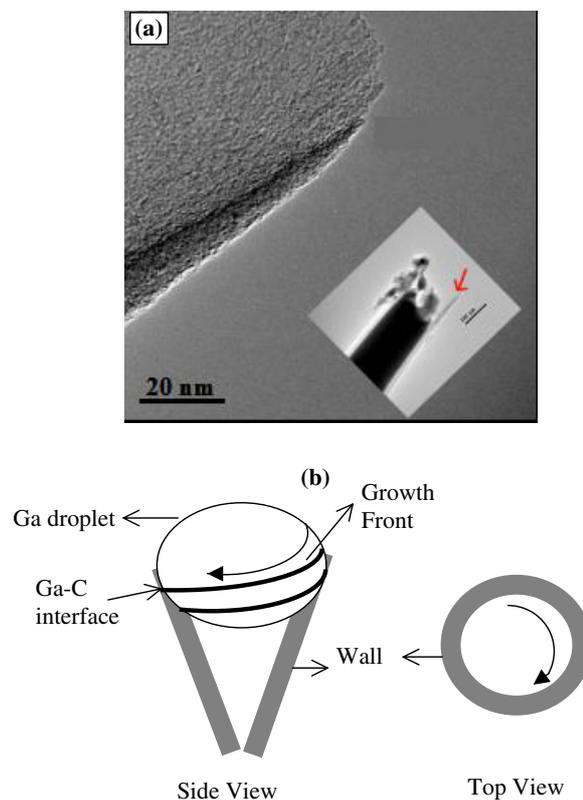


Figure 12. (a) TEM micrograph of the tip of CMT indicating the thinning of wall at the tip. (b) Schematic illustration of the microscopic growth mechanism.

4. Conclusions

This study reports a technique for the synthesis of ‘carbon microtubes’ (CMTs) with large internal diameters and has

illustrated several methods for absolute control of the morphology, internal diameters and conical angles. The ability of gas phase additives (oxygen or nitrogen) in altering the contact angle of gallium with carbon is used to control the conical angle and the internal diameter of the carbon microtubes. Increasing the nitrogen dosing to the gas phase during CMT growth is shown to change the conical angles of the resulting CMTs from $+25^\circ$ to -25° . The walls of the CMTs exhibited a unique structure unlike conventional carbon nanotubes, suggesting a different microscopic growth mechanism. The CMTs with their high density of graphitic nanocrystals should be useful for lithium intercalation and electrolytic capacitors. The CMTs with large internal diameters and conical morphologies at one end should be highly useful for microfluidic applications.

Acknowledgments

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