Growth Model for Carbon Nanotubes

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Evidence is presented, through high-resolution electron microscopy images, for the open-end growth of carbon nanotubes. Terminations of incomplete layers of carbon, seen on the tube surfaces and cone tips, suggest that the extension and thickening of the tubes occur by the island growth of graphite basal planes on existing tube surfaces. The nucleation of positive (pentagons) and negative (heptagons) disclinations on open tube ends results in changes of growth directions, producing different morphologies. A novel structure that shows complete "turn around growth," involving pentagon-heptagon pairs, of the tubular assemblies is presented.

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The recent discovery of carbon nanotubes [1] has added a lot of interest to the field of carbon fiber growth [2–5]. Since the discovery, several reports have suggested the practical usefulness of this material as composites (much better performance compared to any existing graphite fibers), catalysts, and molecular wires [6,7]. Theorists have also concluded that the electronic properties depend on the structure and diameter of these tubes [8,9], making them possible candidates in the electronic industry (for example as molecular switches). The structure of these tubular assemblies of carbon consists of concentric cylinders of hollow carbon hexagonal networks, arranged around one another, often with a helical twist [1]. The tips of the tubes are almost always closed with the presence of pentagons [10] which are positive surface disclinations ($+60°$) in the hexagonal lattice. Heptagons ($-60°$ disclinations) are also seen as important entities in the growth of tubes as they provide negative curvature for the transformation of conical shapes into tubes [10]. But the actual process through which the tubes nucleate, grow, and thicken is still unknown and we shall in this Letter provide answers, unequivocally, to the major questions that are important in the growth process of tubes. The growth process of carbon tubes is unique [4] since carbon is the only elemental material that forms hollow tubes, perhaps due to the strong surface energy anisotropy of graphite basal planes compared to other lattice planes.

The samples used in this study were produced at the negative carbon electrodes during dc arc discharge in inert gas atmosphere and observed in a Topcon 002B transmission electron microscope (TEM) operating at an accelerating voltage of 200 keV. In order to avoid specimen contamination, a newly developed UHV TEM microscope (JOEL-200 FXV) was also used.

In our previous studies [1,10] we had reported that most of the tubes are closed at their ends. However, detailed examination of the samples showed that in rare cases the tubes are seen open at one of their ends [Figs. 1(a) and 1(b)]. The tube growth for these open-ended tubes seems to have been terminated at the ends by some sudden change in the conditions of growth (the carbon species in the plasma are unable to form hexagonal or pentagonal rings to provide further growth or closure of the tube ends). The open ends of the tubes are always covered with some form of carbon residue [the structure looks amorphous; see the images in Figs. 1(a) and 1(b)]. Although it is difficult to tell whether the residue was always present at the growing end or was formed after the tube growth was terminated, it could saturate the dangling bonds of carbon atoms at the peripheries of the open ends. The observation of such open-ended quenched growth structures provides clear evidence for the open-ended growth model (the growing tube remains open at the ends during growth) in comparison to some of the

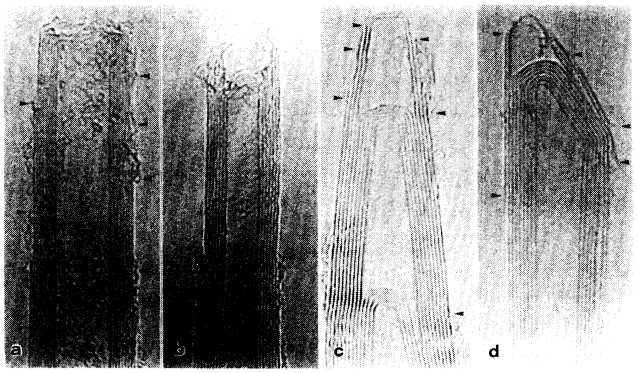

FIG. 1. (a),(b) High-resolution transmission electron micrographs of carbon nanotubes that are observed to be open at their tube ends. Carbonaceous material (amorphous) is seen at the periphery of the open ends of both tubes as well as on the cylindrical surface of (a). However, it is not possible to tell if the carbon residue is inside the hollow or on the outer surface of the tube in (a). (c) Image of a conical-shaped tube end showing incomplete, terminated carbon layers on the surface. The layers are growing from the bottom to the top tip. (d) Incomplete layers on a conical tip, but growing from the tip end to the bottom portion. The terminated layers, forming steps, are shown by arrows in all images. Distance between the layers in all micrographs is 0.34 nm.

closed-tip models, suggested for the case of fullerene molecules and their derivatives [11] and tubes [12].

The tubular assemblies reported before consisted of one to many layers and one of the pertinent questions regarding growth is how the tubes grow in thickness by adding outer layers. Figures 1(c) and 1(d) show clear evidence for the island growth of carbon layers on existing conical tube surfaces, growing from the bottom towards the tip end in Fig. 1(c) and in the opposite direction in Fig. 1(d). The incomplete layers are also seen on the cylindrical surfaces of Figs. 1(a) and 1(b). The images show terminations of the (002) lattice fringes corresponding to the graphite basal planes, forming steps on the tube surfaces, as indicated by arrows. The terminated regions are, again, seen contaminated with carbon residues, suggesting that they are growth regions. The terminated layers are not commonly observed in the samples (as for the case of open ended structures), suggesting that growth is usually completed extremely fast. Oftentimes the nucleated rafts of carbon layers are seen to curl around to form extremely small tubular shapes [13]. The island growth of carbon on tube surfaces and cone tips produces various morphologies (thickened tubes, cones, and stacked morphologies) as observed in the images [1,10]. From various observations we conclude that the island growth is initiated at different points (of special significance as discussed below and later) on the tube surface simultaneously, which later coalesce to produce the completed layers. Since there is a complete registry between the inner and outer layers of the tubular structures, including at points of topological difference (pentagons and heptagons), we believe such points act as nucleation sites for island growth during the evolution of the morphology. Considering the geometry of the structures and the relative abundance of hexagons in comparison to pentagons or heptagons produced during growth, the registry of outer layers with inner ones is easily achieved if nucleation starts at such special points on the tube surfaces.

The roles of pentagons and heptagons are very important in the growth of tubes that are essentially made of a carbon hexagonal network. The nucleation of pentagons ($+60°$ disclination [10,14]) at the periphery of the open ends of growing tubes induces closure of the tubes. So the formation of pentagons is detrimental to the growth of long parallel tubes. Heptagons ($-60°$), in contrast, introduce negative curvature and can reverse the cone shape to cylindrical and annul the effect of pentagons. Hence, in effect, heptagons aid in the growth of tubes by opening up the growing tube ends. In either case, the nucleation of pentagons and heptagons changes the direction of growth in a growing tubule by introducing curvature. The morphology reported in Fig. 2, quite commonly observed in our samples, provides a striking example for the effect of pentagons and heptagons in nanotube growth. The structure can be divided into two parts [see the images in Figs. 2(a) and 2(b) and also the schematic in Fig. 2(c)]: The inner tube with smaller diameter, that

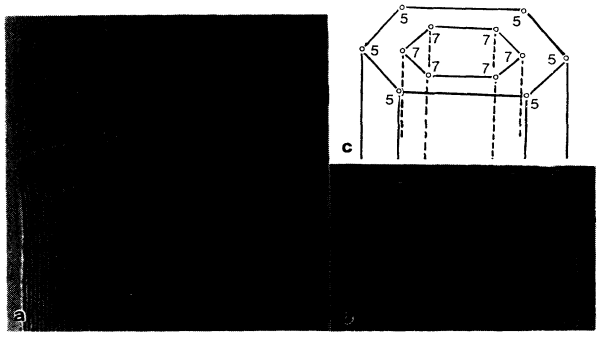

FIG. 2. (a),(b) Images showing the morphology of "turn around growth." The center of the shell (bottom thick part) in (a) is a long tube that extends out of the capsule, whereas in (b) the inside is empty. (c) Schematic of the structure of the capsule (only one layer is shown, corresponding to two parallel fringes in the images) showing hexagonal symmetry along the tube axis and the position of six pentagons (indicated by 5's) and six heptagons (indicated by 7's) resulting in a completely wrapped around double-walled shell. As seen from the schematic, it is essential for the pentagons and heptagons to occur in pairs in order to produce such a structure. The parallel fringes in images have a separation of 0.34 nm.

extends from top to bottom [Fig. 2(a)], consists of only hexagons. But the outer thick shell that wraps the inner longer tube in Fig. 2(a) and the hollow in Fig. 2(b) shows evidence for what we call the "turn around growth." This outer double-walled shell (only one shell is shown in the schematic) has a hexagonal symmetry along the tube axis (shown in the schematic) and consists of six pentagons (outer rim) and six heptagons (inner rim), occurring in pairs. This structure is in fact a variant of the saddle structure where the presence of heptagons and pentagons in pairs leads to the continuation of the lattice with a step, but in the latter the lattice extends in the same direction whereas in the structure reported here there is a complete reversal of the growth direction. Chemically, the presence of adjacent pairs of pentagons and heptagons should be unstable against recombination to form two hexagonal rings, but in the case reported here the two defects are well separated (of the order of the wall thickness of the outer shell). The example reported here should provide experimental evidence for one of the rare cases of existence of disclination pairs, of opposite sign and equal strength, in carbon structures. A similar structure and its stability have been recently discussed, theoretically, where the fullerene tubules are joined together by incorporating pentagon-heptagon pairs [15]. The presence of heptagons or negative curvature in carbon structures has also been pursued theoretically [16,17].

As mentioned briefly earlier, the pentagons and heptagons are special points on the curved hexagonal lattice of the tubular assemblies and the presence of these special points (as local perturbations) should make the tubes

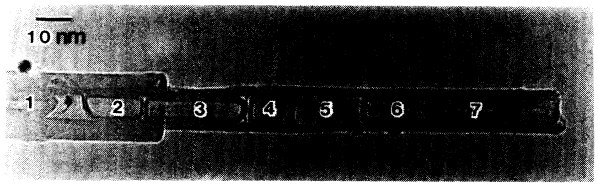

FIG. 3. Log-magnification image of a tubular structure with many completely closed tubules stacked inside (numbered 1 to 7). The structure has one open end suggesting that it is growing towards that end. But in either direction (shown by long arrows) the tube walls have thickened, in the direction of growth, for the numbered stackings (4 is thicker than 5 and 7 is thicker than 6), suggesting that thickening of walls from the inside (as well as outside, from Fig. 2) occurs during growth. The thick left portion of the structure is similar to the one discussed in Fig. 2. The dark blobs seen in the image are carbonaceous contamination.

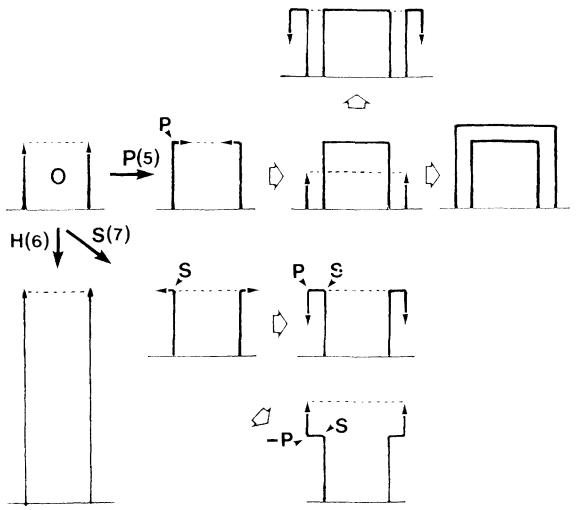

FIG. 4. Schematic showing the various growth probabilities starting from a nucleus O by the addition of hexagons [indicated by $H(6)$], pentagons [$P(5)$], and heptagons [$S(7)$]. Addition of only hexagons to the periphery of an open tube causes growth into longer tubes with no defects. Thickening of the tubes occurs by island growth of fresh layers of graphite basal planes. Successive addition of pentagons causes closure of the tube ends, and of heptagons, an opening up. Notice that the addition of a single pentagon (P or $-P$) can change the growth direction by 90°, but can result in either (P) the "turn around growth" morphology discussed in the text (but six pentagon-heptagon pairs are needed to produce the complete structure) or a step ($-P$) on the surface.

practically viable in applications such as catalysis. We have already seen evidence for carbonaceous decorations at the heptagonal sites and we believe that it will be possible to decorate the tube surfaces, specifically (at the pentagon or heptagon sites), with materials of different chemical significance.

It has also been seen from the structure of tubes that the formation of a stacked morphology, with many completely terminated shells inside the tube hollow, is common (Fig. 3). In Fig. 3, the inside tube has grown out of an envelope (left portion), but contains within stackings of many completed tubules and has an open end at one end (right). It is evident that the inside of the tube has thickened (added more layers) at some stage of growth (see also the figure caption), in either possible growth direction (long arrows). This establishes the open-ended growth model beyond doubt, since it would be impossible for the inside walls to thicken if the tip of the growing tube were closed during growth, but it also shows that diffusion of carbon species occurred through the hollow channels of carbon nanotubes during vapor phase growth. This is also evident in some of the images that we have observed, at junctions inside outer tubules, where the closure of the inner tubular stackings has occurred with inside wall thickening.

In short, summarizing the various observations above, we present the growth model for carbon nanotubes with the help of the schematic in Fig. 4. Starting with a nucleus (O) in Fig. 4, various tube morphologies result (follow arrows) depending on the formation of hexagonal, pentagonal, and heptagonal rings on the periphery of open tube ends. The thickening of the tube structures occurs mainly by island nucleation and layer-by-layer growth on the outer surface of the growing tubes, but the inside surfaces can also thicken to form nested structures inside. A similar process can also be applied to the growth and termination of cone shapes, often seen at the tips of tubes [10]. It is seen that in most cases it is only the inner tube that is important in deciding the morphology of the final structure and the outer layers follow the topology of the inner ones. We believe that pentagons and heptagons on the tube surfaces are special points, topologically, which act as nucleation sites for layer growth of graphite planes or, as reactive sites, for chemical decorations that may be useful in catalysis. The scheme of the outer layers following the topology of the inner structures is perturbed only when the inner tubules change the direction of growth by incorporating pentagons whereas the outer ones grow by adding hexagons, or when a heptagon is nucleated on the growing outer layer. However, it is seen in thick nanoparticles that the position of pentagons falls slightly out of registry as more layers are added, with a meandering of the pentagon sites observed in the final structure.

There are other issues of importance that we have not considered in the growth model presented here, such as the role of helicity in the growth mechanism. As we recently pointed out [18], the helicity in the hexagonal sheets on the cylindrical tube surface is manifested by the exact distribution of pentagons at the tip surfaces of the tubes. Some of the tubes with symmetric tips do not show helicity. The extremely rare occurrence of these structures with symmetric tips suggests that helicity does

play a role in aiding tube growth. We have no evidence yet to suggest the direct role of helicity in growth. We have not talked about the nucleus for growth, but the presence of a large number of nanoparticles along with tubes suggests that these might be precursors in growth [18]. The exact conditions that favor the formation of five-, six-, and seven-membered rings during growth are an important factor that would actually control the morphology of the tubes grown. These could be elucidated, however, in the future by systematically controlling different conditions used in the production of nanotubes and comparing the morphologies formed under different conditions. This should become possible due to the recent progress in the large-scale synthesis of carbon nanotubes [19].

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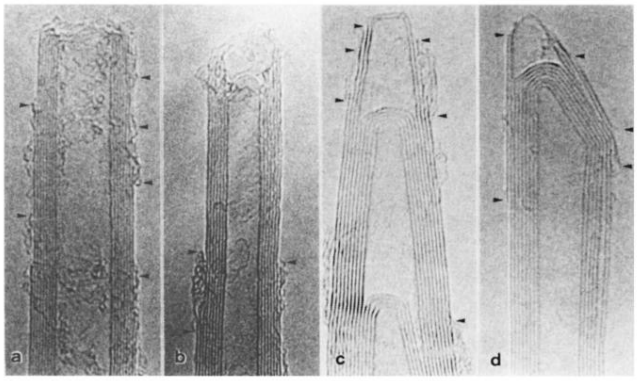

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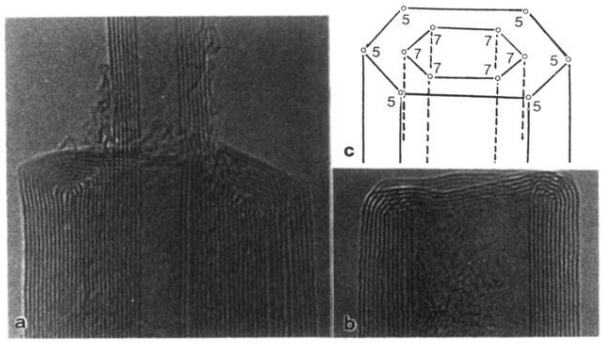

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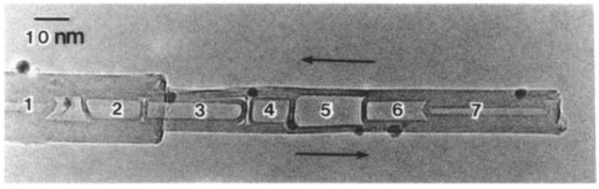

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