

## Self-Assembly of Tubular Fullerenes

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Carbon nanotubes in the form of multiwalled fullerenes are shown here to self-assemble under homogeneous gas-phase conditions of carbon condensation in an inert atmosphere heated to 1200 °C—conditions previously thought to be optimal only for the annealing and growth of C<sub>60</sub> and other spheroidal shells. Tubular fullerenes are known to be less stable than their spheroidal counterparts and have thus far been reported only in circumstances where some extrinsic factor (e.g., high electric fields, catalytic metal particles, hydrogen atoms, or a surface at low temperature) was available to help keep the fullerene structure open at its growing end. The experimental evidence reported here now indicates that multiwalled tube growth is *inherent* in the condensation of pure carbon vapors. Adatoms bonded between edge atoms of adjacent layers at the growing end are proposed to be the crucial intrinsic factor facilitating tube growth by stabilizing the open conformation against closure. This new view of the growing nanotube tip structure is likely to impact on nanotube growth mechanisms under other conditions, particularly the arc.

### Introduction

While advances have been made in elucidating the mechanisms for single- and multiwalled nanotube formation under a variety of conditions, a complete picture has not yet emerged.<sup>1,2</sup> A detailed understanding of nanotube growth is essential to the design of a rational synthesis in which control is gained over such parameters as defect frequency, number of layers, helicity, length, and purity. In fact, one of our group's goals has been to grow, starting from a nanotube seed crystal, a single, continuous, defect-free nanotube fiber to any desired length. Since the production method that currently produces the longest, most perfectly formed nanotubes is the dc carbon arc<sup>3</sup>, we based our attempts at such growth on mimicking arc conditions, but with far greater *control* on such parameters as the tip temperature, continuity of growth, and the adjacency of other nanotubes which otherwise lead to extensive sintering and consequent tube damage.

It was originally proposed by one of us (R.E.S.)<sup>2</sup> that the essential feature of arc growth was the high electric field that concentrates at the growing nanotube tip: the field would stabilize the open tip conformation or increase the barrier to closure. This prompted *ab initio* structure calculations of single-

walled carbon nanotubes in high applied electric fields which indicated<sup>4,5</sup> that stabilization of the open tip conformation is, in fact, obtained as the electric field strength is increased, but this effect alone is not sufficient to make the open form more stable than the closed form of the nanotube at any field less than 10 V/Å. Some other factor must be acting in concert with the electric field to keep the nanotubes open during their growth on the surface of the cathode in the dc arc. The surprising results reported below have led us to the realization that there is in the special case of multiwalled nanotubes an intrinsic factor that tends to keep the growing end open: chemisorbed carbon atoms which bridge between adjacent layers of the growing tube.

### Experimental Section

A portion of our other work involved ongoing studies of metallofullerenes, which we produced by the oven laser-vaporization method.<sup>6</sup> Upon transmission electron microscopic (TEM) examination of the soot recovered from a control experiment using pure carbon target rods (i.e., no metal), we were astonished to discover tubular fullerenes. The apparatus, shown schematically in Figure 1, consists in a 2.5-cm diameter 50-cm, long quartz tube mounted in a temperature-controlled

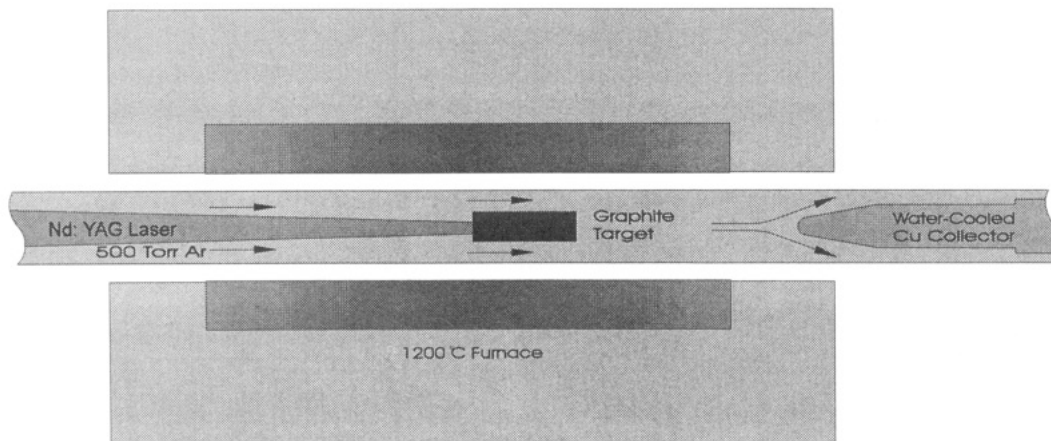


Figure 1. Schematic of the oven laser-vaporization apparatus in which we observed nanotubes for the first time.

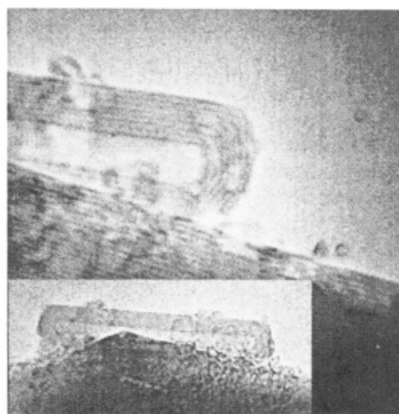
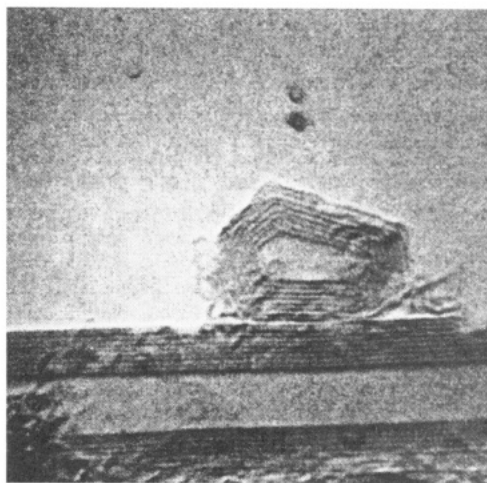
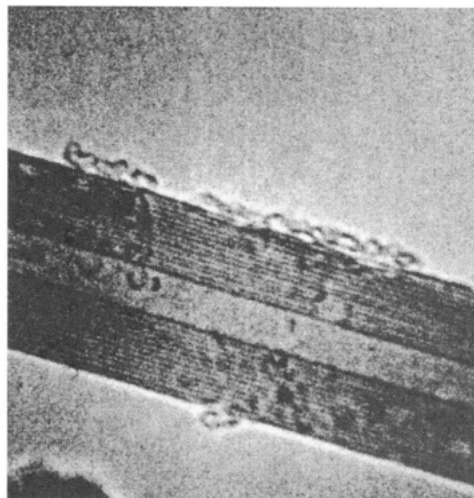
furnace, fitted axially with a 1.25-cm diameter graphite target rod in the middle of the high-temperature zone. After the graphite target (POCO AXF-5Q) target is placed in the tube, the tube is sealed and pumped down to  $<10$  mTorr, and the furnace temperature increased to  $1200$  °C for 4–5 h to outgas the target. High-purity (99.99%) argon is then flowed through the tube at a rate of  $0.2$ – $2$  cm  $s^{-1}$  at a pressure of 500 Torr. The vaporization laser is the second harmonic (532 nm) of a Nd:YAG laser providing 10 ns, 250 mJ pulses at 10 Hz. The nearly Gaussian output beam is focused onto the target using either a 75-cm or a 200-cm focal length circular lens, adjusted to produce a 3-mm or 6-mm beam spot on the target, respectively. The laser beam scans across the target surface under computer control to maintain a smooth, uniform face for vaporization. The argon carrier gas flow sweeps most of the carbon species produced by the laser vaporization, high-temperature condensation process out of the furnace zone, depositing it as soot on a conical water-cooled copper rod.

### Results and Discussion

Nanotubes with 4–24 layers and lengths up to 300 nm were observed (Figure 2) in the soots collected from the water-cooled rod at the end of the apparatus, from the walls of the quartz flow tube and from the downstream face of the graphite target. Even though single-walled nanotubes are readily detectable by TEM, the only single-walled objects found were spheroidal. The yield and quality of multiwalled nanotubes was found to decline as the oven temperature was lowered from  $1200$  °C, when all observed nanotubes were free of defects and closed-ended, to  $900$  °C when defects became increasingly prevalent and finally to  $200$  °C, at which point no nanotubes were observed. Such a temperature dependence is not surprising, since fullerene yield is known to be a sensitive function of the oven temperature.<sup>7,8</sup> Indeed, the original fullerene-producing laser-vaporization experiments of 1985 were performed at room temperature,<sup>9</sup> where the yield of soluble fullerenes has been determined by high-performance liquid chromatography to be 0.01%,<sup>10</sup> while at  $1000$  °C the yield rises to 1–10% (depending on laser spot size) and to over 30% at  $1200$  °C. This behavior is readily explained by the need for sufficient temperature to rapidly anneal the graphene sheet into a closed form through the incorporation of pentagons.<sup>7</sup> It is therefore puzzling how under such facile annealing conditions (i.e.,  $1200$  °C), a nanotube precursor would grow into a long tube rather than closing off into an energetically more stable<sup>11–15</sup> spheroidal fullerene.

The absence of single-walled nanotubes in the experiments described here provides the key to resolving this puzzle. Whereas single-walled objects certainly anneal and close readily at  $1200$  °C to form spheroidal fullerenes,<sup>6,7</sup> open multiwalled species have other alternatives and thus may be quite different in this respect. In particular, for multiwall species it is quite likely that the presence of the outer walls stabilizes the innermost wall, keeping it open for continued growth.

One likely gas-phase mechanism is shown in Figure 3. Here we suggest that the key is the presence of carbon adatoms bridging between adjacent edges of the growing multilayered graphene sheets (Figure 4) thereby prolonging the lifetime of the open structure. Tight-binding calculations of such structures<sup>16,17</sup> indicate that a bridging site is energetically preferred by a quite substantial 0.5–1.5 eV per adatom over any chemisorption site directly above one of the layers, with variations depending on the relative orientations and diameters

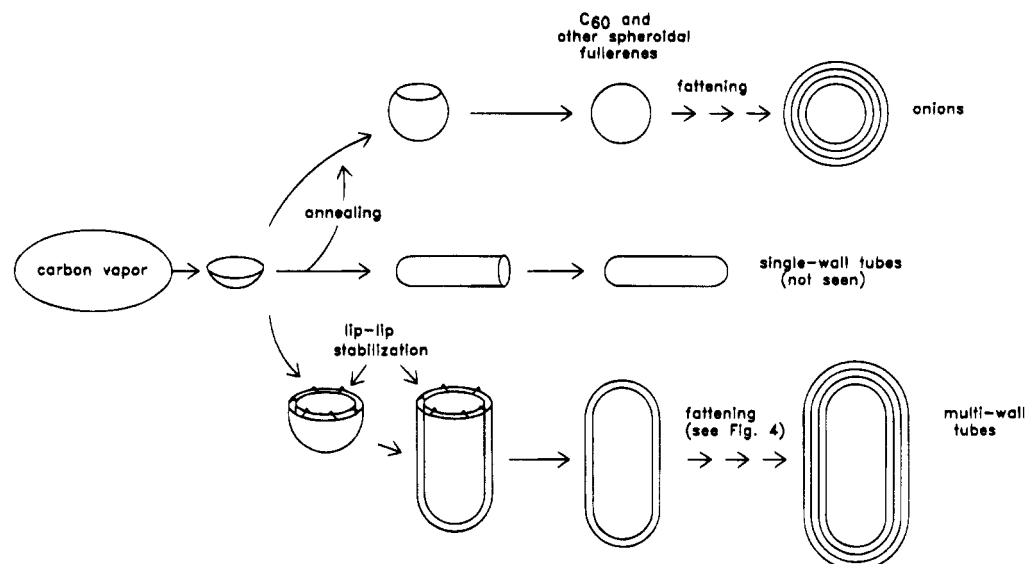


**Figure 2.** Transmission electron microscope (JEOL 2010 operating at an accelerating voltage of 100 kV) images of typical laser-vaporization grown nanotubes. (a, top) A 14-layer nanotube with a 2.7 nm inner diameter. The spheroidal structures surrounding the nanotube may be giant fullerenes or their remnants. (b, middle) A 9-layer nanotube with a 3.4 nm inner diameter adhering to an eight-layer "nanocapsule", i.e., a slightly elongated structure that closed before substantially lengthening. (c, bottom) The tip of an 8-layer nanotube with a 2.5 nm inner diameter. In the inset of a lower magnification view of the entire nanotube shows that both ends are closed. No vestigial structures were observed inside any nanotubes, eliminating the possibility that nanotubes were formed by overcoating incomplete onions. The number of layers ranged between 4 and 24, and the inner diameter varied between 1.5 and 3.5 nm. A prevalence of nanotubes with an even number of layers was observed: 18 of 26 imaged tubes had an even number of layers, compared with arc-grown nanotubes, which yielded 20 even-layered tubes of 39 total.

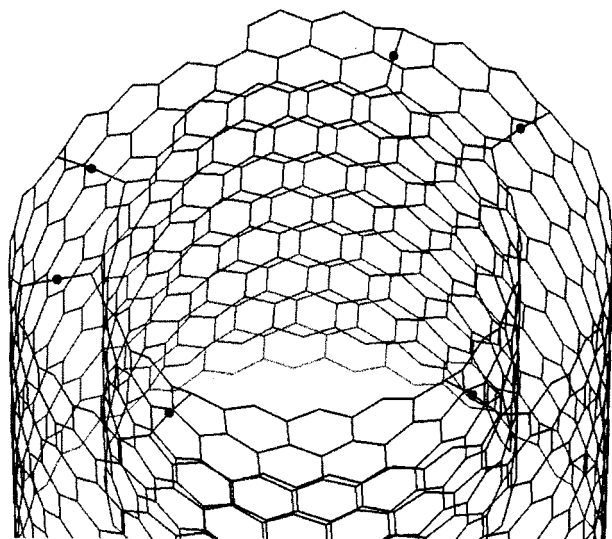
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**Figure 3.** Fullerene branching paths. An initial graphitic flake containing at least one pentagon forms in the condensing vapor. At sufficiently high temperature, it may anneal to a closed fullerene (upper branch), which may subsequently nucleate overlayers, leading to "onions"; both are observed in abundance in the laser-vaporization apparatus. If the carbon density is high, the open shell will sometimes nucleate a second layer before either closes, an adatom "spot-weld" that stabilizes the open conformation will slow the rate of closure. During this period, carbon feedstock from the high-density vapor plume adds to the open edges to form the body of the nanotube. Additional outer layers may then grow by island nucleation<sup>32</sup> and anneal on the underlying nanotube template. Thickening by overlayer growth terminates when the adsorption energy of atoms and small clusters, which decreases with increasing tube or cap radius, falls below the thermal energy of the adsorbate, leading to its desorption. The central branch indicates that without spot-welds to stabilize the open structure, rapid annealing to fullerenes prohibits the formation of single-wall nanotubes, in accord with their absence in the present experiments.



**Figure 4.** Schematic representation of a multiwalled nanotube with an open zigzag tip. Only two of many layers are shown for clarity. Several "spot-weld" adatoms are shown occupying sites between doubly coordinated edge atoms of adjacent layers. Tight-binding calculations indicate that such positions are energetically preferred by 0.5–1.5 eV over direct addition to a layer, depending on the relative local orientation of the layers. We propose that nanotube growth is enabled by adatom spot-welds which stabilize the open conformation.

of the bridged layers. This is such a substantial energetic advantage that there is little question that these adatom "spot welds" and similar structures bridging between the layers are unavoidably involved in the kinetics of nanotube growth whenever the growing ends of multiple layered tubes are adjacent.

This model of nanotube growth in the laser-vaporization apparatus predicts that nucleation and growth of multiwalled nanotubes will increase with carbon density in the initial vapor plume, since within the model it is necessary for the second

layer to form prior to the first's closing, and such will occur only when the feedstock density is sufficiently high. Indeed, shrinking the laser spot size on the graphite target from 6 to 3 mm diameter while keeping all other conditions the same was found to significantly increase the yield of nanotubes. If the carbon vapor density is sufficiently high, as affected by a tighter laser spot, then not only will the high condensation rate promote formation of nucleating open structures with multiple layers, but addition of carbon to the open edges will be rapid enough to lengthen the structure before it finally anneals closed. This argument also accounts for the relative absence of multiwalled nanotubes in the soot collected from the walls of more conventional fullerene generation methods such as resistive heating<sup>18</sup> or carbon arc<sup>6</sup> in the region where the temperature is within the annealing window (i.e., hot enough to anneal the tube structure but cool enough to delay closing until lengthening can occur), the carbon density is too low to nucleate and substantially lengthen multiwalled nanotubes.

The observation of only closed tube tips at 1200 °C indicates that growth terminates at a very short distance from the nascent plume of carbon generated by the laser pulse. This result, together with the retrieval of nanotubes on the cold collector, which is not in contact with the quartz tube, leads us to conclude that their formation most likely occurred homogeneously in the gas phase. We emphasize, however, that the need to invoke an intrinsic stabilizing factor (spot-welds) would persist even if the nanotubes were formed on the wall of the quartz tube, rather than in the gas phase, since the walls are also above the annealing temperature. Such stabilization of the open growing tip may also be critical to the growth of multiwalled tubes under other conditions. As discussed above, the electric field is not by itself capable of stabilizing the open tip under arc conditions, but the calculations that reveal this have been done only for single-walled tubes. The open ends of multiwalled nanotubes growing under actual arc conditions may have enough bridging adatoms which, in combination with the high electric field,

provide the stabilization required to keep the tube tips open long enough to allow formation of these especially long nanotubes.

In sum, the experimental and computational results presented here demand a view of the multiwall nanotube tip structure in which the open tip edges are stabilized against closure by adatom spot-welds bridging between adjacent layers. Of course, single-layer species cannot benefit in this way, accounting for our not having observed any single-wall nanotubes despite temperatures known to be sufficient to anneal carbon clusters to closed fullerenes. This picture of the nanotube tip structure now also impacts on any proposed growth mechanisms for methods of multiwalled nanotube formation in which extrinsic factors, such as a high electric field,<sup>1,19-21</sup> a surface well below the annealing temperature,<sup>22,23</sup> hydrogen atoms,<sup>24-26</sup> or catalytic metal particles,<sup>27-31</sup> are available to keep the tip open. Finally, a realistic understanding of the open nanotube tip structure, in which spot-welded adatoms stabilize the open configuration, is crucial to the rational design of conditions to control nanotube growth from seed crystals, as was the original motivation of this work.

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