

# Carbon rings and cages in the growth of single-walled carbon nanotubes

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We present a growth model for single-walled carbon nanotubes (SWNTs) based on experimental observation and energetic considerations. Carbon rings, observed experimentally and suggested to be fullerene precursors, are the templates for SWNTs nucleation. SWNTs grow by addition of  $C_2$  radicals to catalytically induced reactive sites. This model is consistent with known experimental results and explains the characteristic diameter distribution of SWNTs as resulting from the gas-phase distribution of carbon ring isomers. © 2000 American Institute of Physics.

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## I. INTRODUCTION

Single-walled carbon nanotubes (SWNTs), discovered in 1993,<sup>1,2</sup> have stimulated many efforts to find novel properties of nanoscale materials.<sup>3-5</sup> Progress in this field, however, relies on large-scale synthesis of SWNTs with specific structures. An understanding of the growth mechanism of SWNTs is needed for the design of such a process to produce SWNTs with desired structure and property. Here we present a growth model based on an analysis of experimental observations and energetic considerations. Our model provides a detailed description of the molecular interactions and explains the unique growth properties of this fascinating material.

The most efficient techniques for producing high quality SWNTs (i.e., relatively defect free, large aspect ratios, and exclusively single-walled) in large quantities to date are the arc<sup>1,6-10</sup> and the laser methods.<sup>11</sup> Less well-controlled processes produce SWNTs rooted from catalyst nanoparticles,<sup>6</sup> or generate a mixture of single- and multiwalled carbon nanotubes.<sup>12,13</sup> Since most of the novel properties of SWNTs are based on the molecular perfection of these tubes, we focus on the growth mechanism for arc and laser produced SWNTs, whose properties have been studied most thoroughly.

## II. EXPERIMENT AND RESULTS

We produced SWNTs with various catalysts and promoters using an arc. Fe and Co were used as catalyst while S, Bi, and Pb were used as promoter for producing SWNTs with varying ranges of diameters. The arc was generated with 25 V supply voltage and 95 A dc current under 400 helium atmosphere with 2% to 6% (atomic) of catalyst and promoter. Figure 1 is a typical high resolution transmission electron microscopy (HRTEM) image of SWNTs produced with this method. We measured the diameter distributions of SWNTs produced with different catalysts and promoters and found that, in general, SWNT diameter distributions are narrowly peaked between 1 and 2 nm, a distribution commonly obtained regardless of the synthetic process used.<sup>2,11</sup> Different combinations of these catalysts and promoters, or changes in the reaction temperature, produces modified distributions,<sup>14</sup> although the peak position remains in the

neighborhood of 1–2 nm. The addition of a catalyst promoter tends to broaden the diameter distribution,<sup>7,15,16</sup> as shown in Fig. 2(a). The existence of a characteristic diameter distribution, however, suggests that a unique molecular mechanism accounts for the specificity of the product.

## III. DISCUSSION

No SWNTs rooted from catalyst particles were found in a careful examination of hundreds of transmission electron microscopy images of SWNTs. Similar observations have been found using the laser method.<sup>17</sup> In addition, the diameter distributions do not vary with the overall amount of catalyst. In fact, a high percentage of catalyst loading (>5%) seems to hinder SWNT growth. Also noted is that no SWNTs were found in the center of cathode deposit where the multiwalled carbon nanotubes (MWNTs) form. This leads to the conclusion that SWNTs grow in the gas phase, and the nuclei for formation are a vapor phase species. The root-growth mechanism,<sup>18</sup> which describes growth of nanofibers synthesized from supported catalysts, fails to explain the characteristic diameter distributions of SWNTs synthesized with either arc or laser. A list of experimental observations and their implications is tabulated in Table I.

Carbon rings, observed experimentally to be the dominate species for small carbon clusters ( $C_n$ ,  $n < 40$ ),<sup>19,20</sup> are the logical nucleation species for nanotubes.<sup>21</sup> SWNT diam-

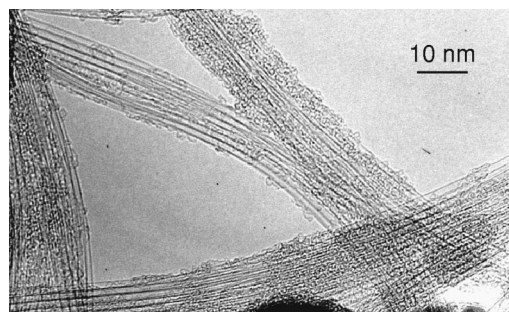


FIG. 1. High resolution transmission electron microscopy image of single-walled carbon nanotubes (SWNTs).

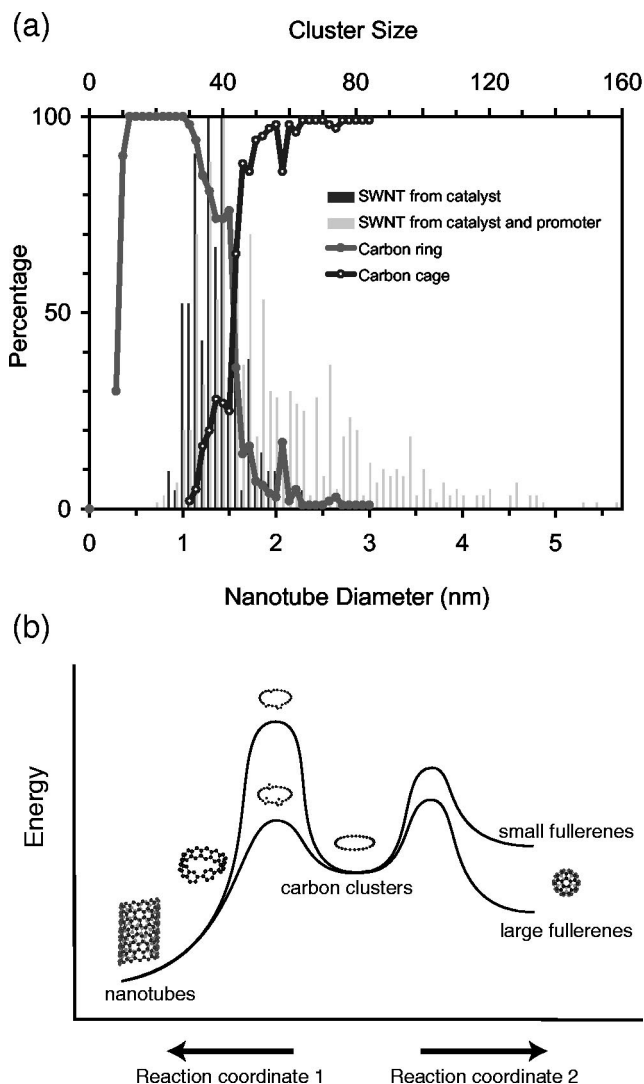


FIG. 2. (a) Correlation between the diameter distribution of SWNTs and the observed gas-phase cluster size distribution. Carbon cluster isomer distributions are represented by circles (from Ref. 41). For small carbon clusters  $C_n$ ,  $n < 40$ , planar carbon rings are the dominate isomers. The probability of fullerene formation increases with  $n$ . Since carbon rings are the nuclei for carbon nanotubes, nanotubes diameters are controlled by the size of carbon rings they grow from. This is demonstrated by the correlation between the histogram of diameters of SWNTs (produced with catalyst only, black bars) and the percentage of ring isomers. Adding promoter increases the lifetime of carbon rings, thereby raising the probability of forming, especially, large diameter nanotubes (gray bars). This mechanism make it possible to grow nanotubes from large carbon rings, with fullerene formation as a competing reaction channel. We used the average ring size (described in Table II) to calculate the corresponding SWNT diameter. (b) Reaction pathways of carbon rings to carbon nanotubes and fullerenes. The first step of SWNT growth is nucleation, which is accomplished by the carbon clustering in the gas phase to form planar rings. A transition metal catalyst plays a role in creating sites for subsequent  $C_2$  addition. Without a catalyst, this process requires bending C–C bonds in a planar carbon ring, which is a high energy transition state. To overcome such a reaction barrier, the reaction temperature would have to be extraordinarily high (the upper curve of the reaction coordinate 1). Unfortunately, carbon rings, which are the nuclei for SWNTs, are not stable at such high temperatures. The rings, therefore, pass through a lower transition state to form fullerenes (the reaction coordinate 2). With a catalyst, the reaction barrier is lowered substantially, and the thermodynamically and energetically favored nanotubes formed abundantly (the lower curve of reaction coordinate 2).

TABLE I. Experimental observations and their implications to the growth mechanism of carbon nanotubes.

Experimental result	Implication
Characteristic diameter distribution	Reaction not controlled by thermal stability of the products
No metal particles at the end	SWNTs not grown from metal nanoparticles
Multiwalled nanotubes do not need catalyst	Fast lengthening process possible without catalyst
Catalyst required for SWNT growth	Reaction barrier high without catalyst
Diameter distribution changes with promoter	Reaction controlled by kinetics

eters as large as 2.5 nm are commonly produced with catalyst promoters, such large diameters could form from  $C_{60}$  carbon rings, and rings of this size are known to occur in the gas phase. The model proposed by Thess *et al.*<sup>11</sup> assumes, instead, that SWNTs grow from  $C_{240}$  caps, resulting in a uniform (10,10) tube structure, which is inconsistent with many of the experimental observations<sup>22</sup> and cannot account for a distribution of tube diameters. Moreover, gas phase species with fullerene cap structures have never been observed experimentally.<sup>23,24</sup> Even if one assumes that fullerene caps exist as transient species, one would need to postulate the existence of extremely large fullerenes as large as  $C_{1100}$ . Such large molecular fragments, however, have not been directly observed. A comparison of the size of rings or caps needed to grow SWNTs with different diameters is listed in Table II.

The necessity of catalyst indicates that the reaction barrier is high even compared with the relatively high temperatures in the vicinity of the arc plasma. The role of catalyst is to provide an alternative reaction pathway, which involves a lower energy transition state complex. Cobalt is known to catalyze cyclotrimerization of acetylenes via parallel reaction pathways,<sup>25</sup> and many transition metals also catalyze cyclization of acetylene to benzene at temperatures lower than without catalyst.<sup>26</sup> Similar molecular catalysis may occur in the

TABLE II. Corresponding sizes of carbon rings and fullerenes needed for nanotube growth. The range of ring sizes are calculated by assuming  $n = 2\pi D/[0.142(3/2)]$  (armchair tubes) and  $2\pi D/[0.142\sqrt{3}]$  (zig-zag tubes). Fullerene sizes are calculated by assuming the diameter  $D$  scales with  $\sqrt{N}$ , and the diameter of  $C_{60}$  is 0.7 nm. For example, a 1.2 nm diam nanotubes would require either a  $C_{30}$  ring or a  $C_{180}$  fullerene cap, while a 2 nm diam nanotube would require either a  $C_{50}$  ring or a  $C_{490}$  fullerene. Such a large fullerene is rarely observed, whereas the ring lies in the size range commonly observed in experiments.

D (nm)	Ring size ( $n$ )	Cage size ( $n$ )
0.7	18–20	60
1.0	26–30	120
1.2	30–36	180
1.5	38–44	280
2.0	50–60	490
3.0	76–88	1100
4.0	100–120	2000
5.0	130–140	3100
6.0	150–180	4400

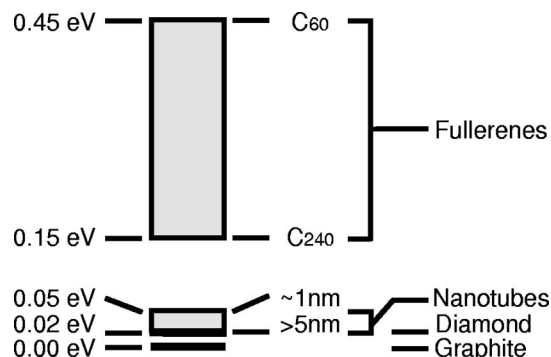


FIG. 3. Energies of different forms of carbon. Although the most stable form of carbon is graphite, carbon nanotubes and fullerenes are produced abundantly under suitable reaction conditions. The formation of SWNTs, therefore, is controlled by kinetics.

gas phase, where the presence of atomic cobalt lowers the reaction barrier for the highly exothermic nanotube formation reaction. According to the Arrhenius equation, the reaction rate constant  $k$  is

$$k = A e^{-E_a/RT},$$

where  $A$  is the constant frequency factor, and  $E_a$  is an empirical activation energy. A decrease in the activation energy or an increase in the temperature have exponentially large effects on the reaction rates. A schematic description of the reaction pathways is illustrated in Fig. 2(b).

Carbon is known to self-assemble into different forms under varying synthetic conditions.<sup>9,27,28</sup> SWNTs form in the presence of transition metal catalysts such as Fe, Co, and Ni at temperatures above 800 °C. Under similar conditions, carbon self-assembles into fullerenes<sup>19,29–31</sup> without catalyst. Vapor-grown carbon fibers, on the other hand, grow from supported-catalyst particles at lower temperatures ( $\approx 600$  °C).<sup>32</sup> The product distribution of carbon self-assembly is, therefore, controlled by the reaction kinetics<sup>33</sup> rather than by the thermal stability of products (see Fig. 3).

Figure 4 illustrates the growth model. A reactive  $C_2$  can

only be added to a non-planar carbon ring, as demonstrated in Figs. 4(a) and 4(b). Bending of C–C bonds does not occur even at temperatures as high as 3000 °C ( $\approx 0.25$  eV). On the other hand, the ring can form a lower-energy, metal catalyst-carbon complex that has lower energy barrier for  $C_2$  addition, as depicted in Fig. 4(c). Once the first belt formed,  $C_2$  can add to the growing edge of the belt and lengthen the tube with or without catalyst, as shown in Figs. 4(d) and 4(e).  $C_2$  as the building block for carbon nanotubes was supported by *in situ* spectral measurements, which indicated a strong correlation between  $C_2$  radical abundance and single-walled carbon nanotube production.<sup>34</sup> Reactive  $C_2$  radicals, though usually not present in the same region where carbon rings would otherwise dominate without catalyst, may be stabilized and transported by the catalyst species to a growing nanotube end. Such free standing, open-ended SWNTs in vacuum have been observed.<sup>35,36</sup>

The promoter plays an important role in stabilizing intermediate species during the nucleation process. Additives such as sulfur have been found to promote the growth of large carbon clusters,<sup>37</sup> which has been attributed to temporal stabilization of the free radical intermediates by chemically tying up dangling bonds. By forming weak bonds with carbon rings, promoters prevent ring folding, thus extending the carbon ring lifetime for tube formation. This mechanism explains why large diameter carbon nanotubes are not observed without a promoter, even though larger SWNTs are thermodynamically more stable (see Fig. 3). The same effect would also help stabilize smaller carbon rings, thereby increasing the total yield of SWNTs, which is consistent with our observations.

Bundling of SWNTs occurs during the growth, since the long polymerlike tubes are entropically unlikely to crystallize after formation. The final product from SWNT synthesis is often a hexagonally packed crystal, and the helix angles are often correlated within a bundle.<sup>38</sup> Short SWNTs must aggregate first, and then the lengthening process continues. According to calculations based on local density approximations, the binding energy between carbon and the tube walls

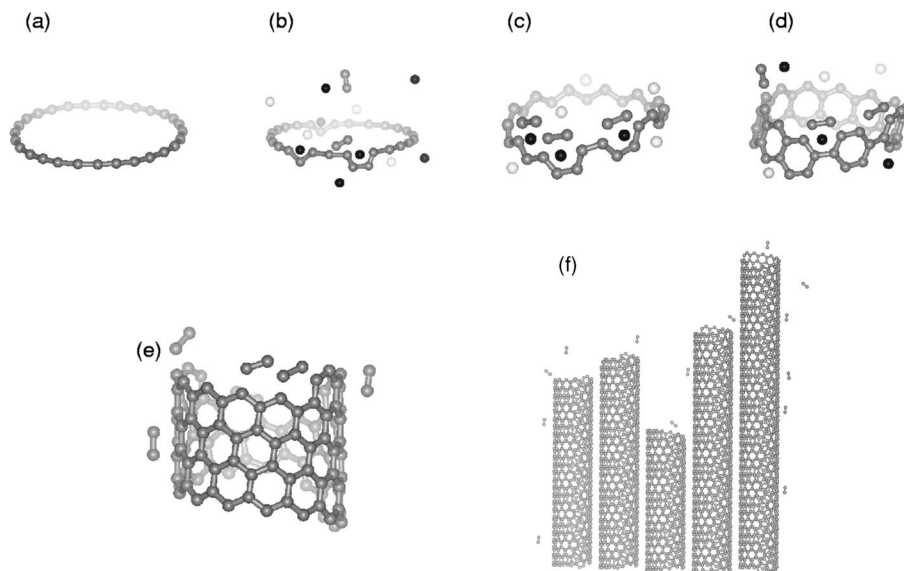


FIG. 4. Growth model of SWNTs. Gray balls: carbon; black balls: catalyst; light-gray balls: promoter. (a) A planar carbon ring is the nucleus for a SWNT. (b) Catalyst creates sites on a planar carbon ring for  $C_2$  addition. (c) Promoters temporarily bind to a carbon ring to prevent it from closing while the catalyst creates reactive sites. (d) The first belt determines the structure of the nanotube. (e) Once the first belt forms, nanotube continue to grow with or without catalyst. (f) Bundling of SWNTs occurs at an early stage of tube growth.  $C_2$  that impact the tube surface will diffuse on the tube wall until reaching the growing edge. Therefore, the outer tubes in a bundle have higher growth rates because of a larger surface area.

is small compared to that of the tube edge.<sup>39</sup> Therefore, carbon atoms and clusters can glide efficiently along the tube surfaces to the reactive end sites, which implies that the tube growth rate should increase with increasing sticking coefficient, rate of surface diffusion, and surface area. As in the case of MWNTs, nanotubes grow with an open end as long as there is a template suitable for C<sub>2</sub> addition, and the outer layers are usually longer than the inner layers.<sup>40</sup> The rate of C<sub>2</sub> addition is very rapid even without a catalyst, as evidenced by the fast growth rate and high yield of MWNTs on the cathode. Figure 4(f) illustrates that a lengthening process similar to that of MWNTs is responsible for SWNT growth.

#### IV. CONCLUSIONS

Our model suggests that SWNTs grow in the gas phase with an open end. Carbon rings are the nuclei, and catalyst and promoter play a crucial role in the nucleation process. This model suggests that keeping SWNTs in the gas phase at elevated temperatures will be helpful for large-scale production. Uniform control of the diameters of SWNTs may be achieved by starting with well-defined templates, which may be synthesized *a priori*.

#### ACKNOWLEDGMENTS

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