Polyyne Ring Nucleus Growth Model for Single-Layer Carbon Nanotubes

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We propose, based on recent experimental results, a polyyne ring nucleus (PRN) growth model for the synthesis of single-layer nanotubes (SLN's). The PRN model assumes that (i) the critical nuclei are the planar carbon polyyne rings that are observed to be most stable for sizes in the range C_{10} to C_{40}; (ii) Co_mC_n clusters (possibly charged) play the role of a catalyst by serving to add C_2 or other gas phase species into the growing tube; (iii) promoters such as S, Bi, and Pb serve to modify the rates for these processes by stabilizing the ring structure. We suggest experiments to test and amplify this PRN model, including a flow tube arrangement that might be useful for synthesizing more uniform SLN's.

PACS numbers: 61.46.+w, 81.10.Bk

Carbon gas phase self-assembly has produced three classes of small carbon fibers: (i) vapor phase grown carbon fibers [1,2], (ii) multilayer nanotubes [3,4], and (iii) catalytically grown single-layer nanotubes [5,6], each of which suggests several interesting applications [7,8]. Current synthetic techniques, however, lead to uncontrolled growth and a jumble of tubes mixed with soot and fullerenes [5,6,9–11]. An understanding of the nanotube formation mechanism is crucial to design procedures for controlling growth conditions to obtain more practical materials.

Single-layer carbon nanotubes (SLN) are produced in an arc between graphite electrodes under a helium atmosphere [5,6]. This same system also produces fullerenes in the soot and multilayer nanotubes in the cathode tip deposit. The SLN's have diameters of 1 to 5 nm, and form only in the presence of a transition metal catalyst, e.g., Fe [5], Co [6], and Ni [10,11]. They are found only on the cold chamber walls (together with fullerenes) and appear to grow in the gas phase. They have closed ends and (unlike vapor grown carbon fibers) do not have metal particles associated with them. In the presence of a Co based catalyst, the promoters S, Bi, and Pb increase the production yield of single-layer nanotubes as well as dramatically modify the diameter distribution [9,12].

The differences in structure and growth environments suggest that the SLN growth mechanism is distinct from that of multilayer nanotubes or carbon fibers. Figure 1 shows the size distributions we observed for single-layer nanotubes produced with Co [9], Co + S [9], Co + Bi [12], and Co + Pb [12]. The sharp variations in the diameter distribution are not understood in terms of tube stability [13,14] or catalytic particle size [9]. Different catalyst promoters increase total yield, but the tubes produced have similar diameter distributions (mostly between 1 and 2 nm) [9,12], which corresponds to rings with 20 to 50 carbons at the circumference.

We believe that planar polyyne rings serve as nuclei for forming single-layer nanotubes. Such ring structures have been observed in carbon vapors produced by laser ablation (and analyzed by drift tube experiments [15–17]). In analyses of carbon vapor aggregates, planar rings constitute the dominant isomers for $n = 10$ to 40, whereas spheroidal species are most prevalent for $n > 40$ [16–18]. If grown from single carbon rings, the SLN diameter would be related to the ring size. Thus C_{32} and C_{38} monocyclic rings would lead to SLN's with diameters of 1.25 and 1.5 nm, respectively, which correspond to the peaks in Figs. 1(a)–1(c).

This polyyne ring nucleus (PRN) model for SLN production explains that small diameter SLN (rarely found on the cathode) are the major nanotube product for cobalt-catalyzed processes. Some workers [15,16] believe that fullerenes grow from carbon rings as follows: small monocyclic rings (C_{10} to C_{30}) coalesce to form polycyclic rings and subsequently convert to either monocyclic rings or fullerenes. The PRN mechanism is compatible with this mechanism, and we postulate that two channels compete for polycyclic ring conversion: fullerenes versus single-layer nanotubes. Hunter et al. [16] comment that the predominance of C_{60} in the mass spectrum is the result of efficient conversion from rings to fullerenes. They conclude that the polyyne rings with more than 100 carbons are not observed in their helium drift tube system because (i) the channel for conversion to fullerenes competes favorably, and (ii) the rings are too unstable energetically to survive at a high temperature. This may be why large diameter SLN's are not observed in the absence of catalyst promoters (S, Bi, or Pb) [5,6,9,10,12].

The PRN model for cobalt-catalyzed growth of SLN's is illustrated in Fig. 2. Figure 2(a) depicts a monocyclic carbon ring and a Co_mC_n species as the starting materials for producing SLN's. In the arc plasma, the presence of electrons and other charged species (carbon and metal
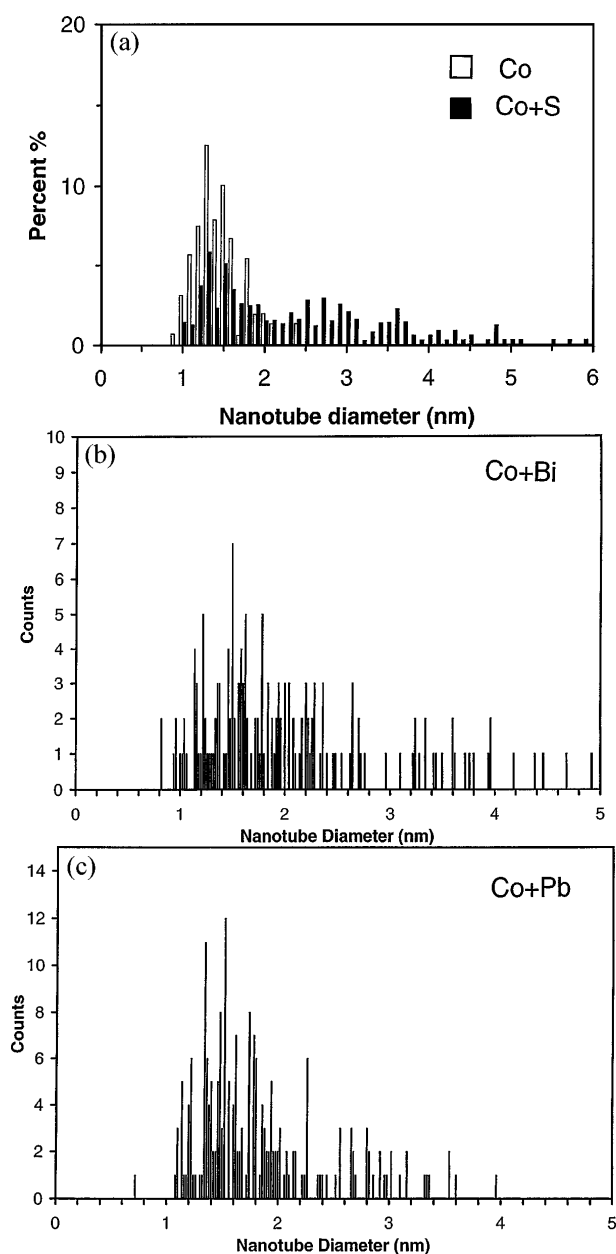
FIG. 1. Histogram for diameter distribution of nanotubes produced with cobalt catalyst and different promoters: (a) Co only (open bars) and Co + S (solid bars), (b) Co + Bi, and (c) Co + Pb.

FIG. 2. Diagrams illustrating the polyyne rings nucleus mechanism for growth of single-layer carbon nanotubes. (a) A monocyclic polyyne ring is the nanotube precursor and a cobalt carbide cluster is the catalyst. The cobalt carbide cluster composition and structure is undetermined, but it should be able to bond to C_n and/or add the C_n to the growing tube. (b) Deformation of monocyclic ring from its planar geometry (due to charges or catalyst), resulting in local *cis* and *trans* forms. (c) Formation of a nonhelical tubule having the armchair structure. (d) Formation of a nonhelical tubule having the zigzag structure. (e) Formation of a helical tubule. After the first benzene ring formed at a *cis* site, growth continues on *trans* sites to generate tubules with helical structures. (f) Formation of a tubule with a different helical structure from that of (e). Growth continue on *trans* conformation follow two C_2 addition at *cis* conformation.

clusters) may cause the geometry of a monocyclic ring to deviate from the uniform planar form at elevated temperatures, resulting in local *cis* or *trans* carbon deformations, as shown in Fig. 2(b). (Deformation of a polyyne chain from its straight geometry has been proposed in the carbyne crystalline form of carbon [19].) The *cis* form provides a building block for adding C_2, carried by the cobalt carbide cluster to the growing site. The SLN's thus formed should have zero helicity with the armchair structure, as shown in Fig. 2(c). We have observed a few tubes with nonhelical armchair structure. A zigzag tubule
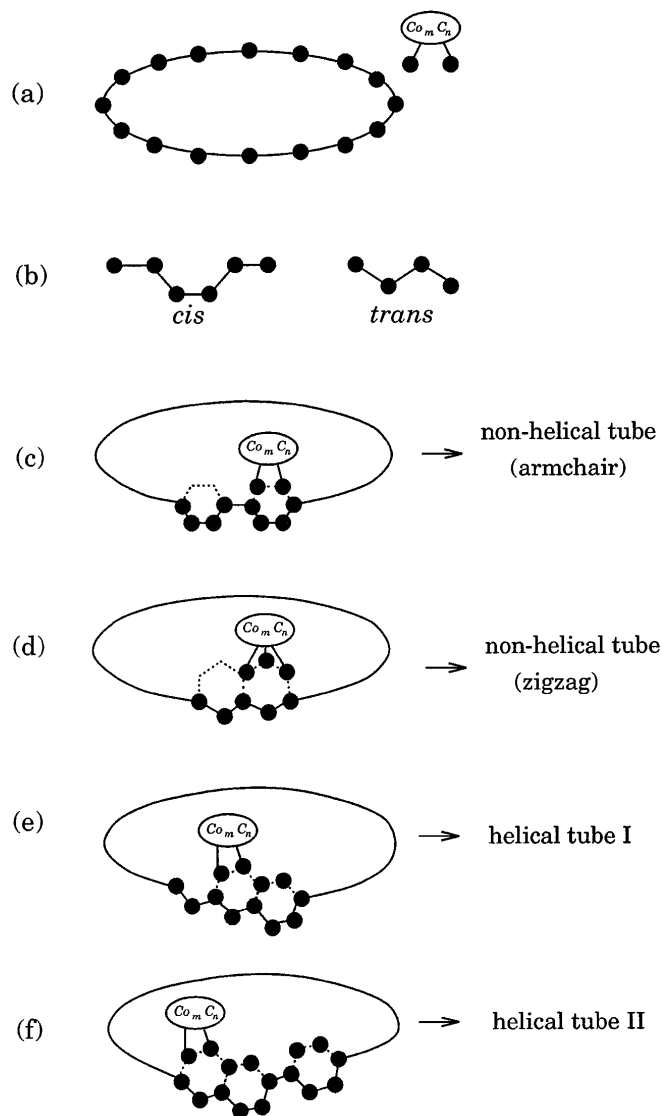
structure, on the other hand, can result by adding a C_3 to a *trans* conformation of the initial polyyne ring [Fig. 2(d)]. Subsequent C_2 species can be added to the *trans* polyyne ring plus benzene precursor. The helical angles are determined by the ratio of *cis* to *trans* conformations of the nucleus during the growth of the first benzene ring

belt. For example, after building the first benzene ring by adding a C_2 to the *cis* site, subsequent C_2 affixing to the *trans* site adjacent to the benzene edge results in a helical tubule, as shown in Fig. 2(e). Alternatively, when a *trans* addition follows two *cis* additions, a tubule with different helical angles forms [Fig. 2(f)].

The experimentally observed lack of additional layers on the catalytically produced nanotubes supports the PRN hypothesis that the nanotubes grow from a polyyne ring gas phase species. We have imaged over 3000 tubes and found only one example of a double-layer tube [9]. This is in contrast to the case of nanotubes formed on the cathode, where multilayer tubes are common, and SLN's have never been observed [3,4]. We suggest that multilayer tubes grow from the cathode, which provides a surface for nucleation of multiple layers [20,21]. The PRN model that polyyne rings present in the plasma serve as growth nuclei is consistent with these observations, since there are no nuclei for forming multiple layers.

The formation of larger diameter tubes upon the addition of S, Bi, or Pb to the Co system suggests that these promoters modify the growth at the nucleation stage. We speculate that these promoters stabilize larger monocyclic rings, providing the nuclei necessary to build larger diameter tubular structures (which grow rapidly into long tubes). The same promotion effect should also stabilize tube growth intermediates, resulting in an increased yield of the final product. However, a definitive answer to the role of promoters awaits a better understanding of all fullerene growth processes.

An alternative growth model for the vapor phase grown carbon fibers has been proposed [1,2], which is based on the observation that the fibers usually include a catalyst particle at the tube end. SLN's grown by the Co catalyst, however, do not contain metal particles [22]. Most SLN's show one end with no particles, while the other end is usually merged in the soot. Close examination of the tubes often reveals that the tubes are lying on top of particles, as seen in Fig. 3. Also shown in Fig. 3 is a small tubule with both ends free of metal particles. We conclude that either the catalytic species departs after closure of the nanotubes (which favors the hypothesis that small metal clusters are the catalyst in nanotube formation), or they must involve sufficiently few metal atoms so as to be undetectable.

Another growth mechanism suggested for growth of carbon nanotubes is the incorporation of carbon dimers into a cagelike precursor [7,8,23]. In this model, the tubule grows from an empty fullerene cage by repeated addition of C_2 to a hemisphere cap. Lengthening of the tubes results from rearranging the carbon bonds to incorporate additional C_2 near a pentagonal ring. Since the growing tubule is always closed, there is no mechanism to enclose materials into the tubule. Thus the cage precursor mechanism is in conflict with the experimental evidence that carbonaceous material is encapsulated in the
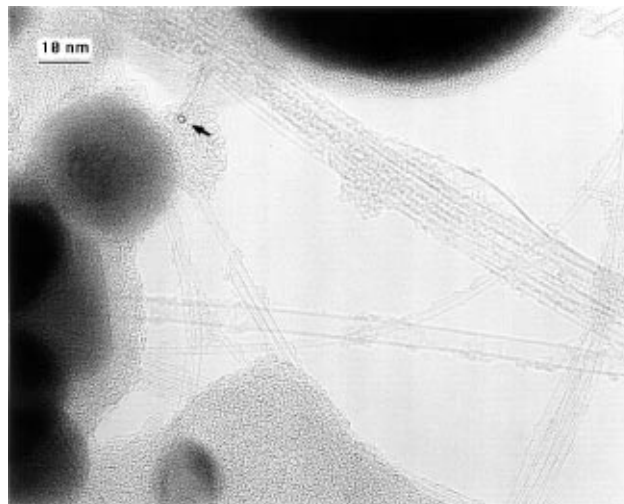

FIG. 3. Transmission electron micrograph of SLN's produced by Co and Bi. The arrow indicates a short nanotube of 0.7 nm diameter with both ends free of particles.

nanotubes. Figure 4 shows one section of a nanotube that has expanded radially to enclose amorphous material, strongly suggesting that the material was included in the tube during the growth. We conclude that the material inside the tube must have been captured during the growth, and only a model with an open growing end is consistent with the observation. By tilting the specimen to view the tubes with various orientations, we have confirmed that some tubes have the amorphous materials inside.

Several aspects of the PRN growth model could be tested experimentally. For example, if carbon vapor and cobalt (or cobalt carbide) clusters having a narrow range of mass distribution could be controlled independently, one could vary the concentration of the proposed active catalytic species and observe the results. Annealing
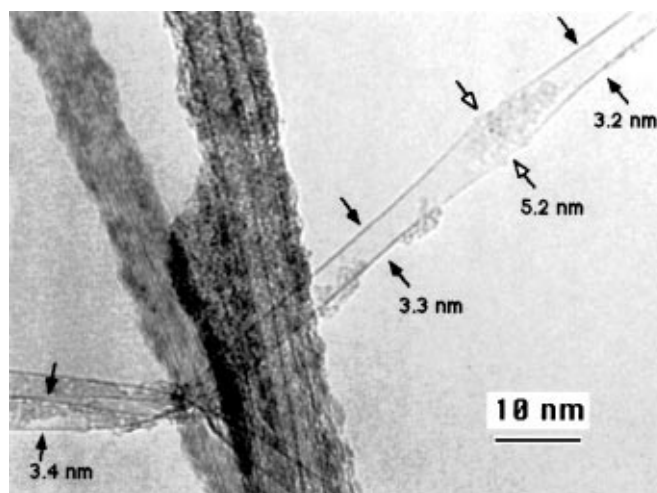

FIG. 4. Amorphous material that has expanded the tube wall of an SLN. This suggests that the amorphous material was incorporated during the growth. This observation supports the mechanism that tubes grow at open ends.

studies of the carbon ring isomer structures in the presence of catalyst promoters would verify the stabilization of monocyclic rings by these elements. Study of cluster mobilities has revealed that there is a group of isomers C_{29} to C_{45} that have a mobility between planar rings and fullerenes [24]. They appear to be three dimensional, and the authors refer to them as open fullerenes. This group of isomers might be the nanotube nuclei which have started to grow.

A flow tube system consisting of a carbon ring source, injection of promoters, and finally the introduction of cobalt carbide species would be useful for synthesizing nanotubes of a well-defined diameter and with higher yield. Such additional information on nanotube and carbon ring formation would allow refinement of the growth model, which might lead to improved synthetic methods.

In summary, the PRN growth model explains several experimental observations unique to the SLN's grown in arcs containing Co catalysts. The single-layered feature is explained, since the nanotubes originate from a carbon ring precursor. Inclusion of materials in the tubes is explained because the growing tube has an open end. The characteristic diameter distributions are explained in terms of stability of the carbon ring nuclei. The abundance of larger diameter nanotubes formed with catalyst promoters is explained by the stabilization of larger ring precursors.

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