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Formation of Carbon Nanofibers

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Recently 3–150-nm-diameter carbon fibers have been discovered which appear to grow spontaneously by deposition from carbon vapor. It is proposed that these structures may be giant fullerenes which have grown by direct insertion into the graphitic network of smaller carbon species (atoms, "linear" chains, monocyclic rings, or even smaller fullerenes) accreted from the vapor phase.

Introduction

Carbon fibers have major industrial applications, and their growth mechanism and the factors which control their structure are of major strategic importance. Some fibers, as discussed by Endo,[1] are known to grow by catalytic intervention of small metal particles which leave hollow cylindrical graphite tubes in their wake. Recently a new type of microscopic carbon fiber has been detected which appears to consist of very small diameter graphite tubes from 3–150 nm in diameter. Iijima[2] has published transmission electron microscope (TEM) images of such fibers which appear to grow on the cathode of a fullerene arc-processor similar to that developed by Krätschmer et al.[3] Similar structures have also been observed by Endo[4] in a carbon fiber generator. The cylinder walls may consist of only a few layers of graphite, 2–5, or as many as 50 or more. Such fibers are an exciting development in submicro/nanometer scale engineering as they may well be the strongest structures so far fabricated. Interestingly these tubes appear to grow spontaneously by accretion of carbon units from carbon vapor at high temperature *without* the intervention of a catalytic metal particle.[2,4] This suggests that pure carbon structures grow spontaneously by some autocatalytic process.

Recently there has been a breakthrough in our understanding the range of structures which can be fabricated solely from an array of sp^2 carbon atoms. This new perspective is based on the discovery of the fullerenes,[5] their isolation and structural characterization,[3,6] and the development of likely mechanisms for their formation.[7–9] Since the discovery, there have been many studies of the fullerenes,[10–12] and, in particular, it has been realized that hollow carbon cage structures may be small with 20–70 atoms[13] or very large with several hundreds to thousands of atoms, as in the case of the giant fullerenes,[8,14] and they appear to form spontaneously. Fullerene-70[15,13,6] is an interesting species in this context as it consists of two C_{30} fullerene-60 hemi-"spheres" connected by a ring of ten extra carbon atoms in the waist. It is clearly possible to add more such rings to produce elongated tubular fullerenes, and Fowler[16] has discussed various theoretical aspects of these structures. Indeed it is noteworthy that Buckminster Fuller patented related "elongated geodesic dome" structures.[17]

The fact that carbon can spontaneously nucleate to form fullerenes is fascinating, and possible intermediates in the formation process were discussed soon after they were found.[7,8] It was suggested that an extended sp^2 carbon network, involving hexagons *and* pentagons must form in some way from smaller carbon species (C_n, atoms, chains, and rings), which may close—driven by the energetics involved in dangling bond elimination. If closure occurs, then fullerenes form; if not, then a spiraling graphite sheet[7] is expected to epitaxially self-wrap[8] itself up to form an onionlike polyhedral graphite microparticle. The quasipolyhedral shapes which the giant fullerenes were found to have[8] provided the key to an understanding of the detailed infrastructures of the spheroidal graphite microparticles observed by Iijima in 1980.[18,19]

The original refined nucleation scheme[8] recognized that multiple shell closure by (delayed) annealing—resulting in shell entrapment—could be important under certain conditions. However as perfect closure did not appear to be particularly effective in the formation of the spheroidal particles seen originally by Iijima,[18,19] the scheme[7,8] focused mainly on conditions where annealing was not important and explained the interconnected shell infrastructure observed in these particles. Carbon nucleation is complicated, and it is clear that the range of species produced depends critically on the temperature, pressure, nucleation time, and, in particular, the homogeneity of the physico/chemical environment as well as the intrinsic equilibrium of the nucleating system. (Note: In the case of carbon fiber growth, especially if attached to a surface, inhomogeneities will give rise to anisotropic growth. Under some gas-phase conditions, only small radicals form;[20] under others, microparticles form;[18,19] and under yet other conditions, closure to form fullerenes may be the dominant process.[21] Nanoscale fiber formation[2,4] appears to be yet another facet of carbon's apparently limitless synthetic engineering capability, and the purpose of this paper is to draw attention to the fact that

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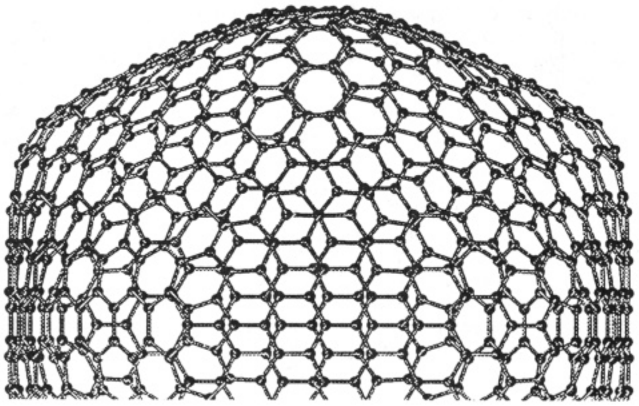

Figure 1. Computer simulation of a giant fullerene end cap.[24] The structure has been relaxed by molecular mechanics.

there is a close relationship between the fullerenes and these fibers; in particular their structures and formation schemes show many features in common. The present study is based on a comparison between transmission electron microscope (TEM) images of nanoscale carbon fibers[2,4,22] and a theoretical investigation of the structures of giant fullerenes and related quasiicosahedral graphite microparticles and the resulting simulated TEM images.[23-25]

Observed and Simulated Carbon Nanofiber Structure

Apart from the beautifully cylindrical structures of the recently observed nanofibers, the most striking result is the fact that the TEM images show that the ends are capped by a continuous dome of carbon.[2,4,22] Iijima states[2] that the microfibers he has observed are "usually closed by caps which are curved, polygonal or cone-shaped", and examples are presented (see ref 2, p 18). The discovery that giant fullerenes have quasiicosahedral shapes[8] readily explains these discoveries as it shows how a closed graphite network may give rise to caps with a wide range of shapes and in particular those observed. Simulations of the TEM images for giant fullerenes have been made[23-25] which confirm Iijima's observation[19] that when four to five carbon atoms lie in some structural relation, within a 0.2 nm thick wall alligned parallel with the electron beam, a dark line TEM image is produced. This enables the *outlines* of graphitelike polyhedra to be observed in TEM images. The simulation studies[23-25] indicate how a wide range of shapes for such caps might occur. The shape observed depends not only on the actual 3D shape of the fullerene but also quite critically on the orientation of the object in the electron beam.[23] In Figure 1, a computer generated carbon network for a symmetric giant fullerene half-dome is depicted. In its simplest (and *ideally* (!) symmetric) form a microfiber would be capped by a continuous network of sp^2 carbon atoms which can be achieved most readily by the inclusion of six pentagonal configurations. In the most symmetric configuration (Figure 1), a single pentagon lies at the apex and five further pentagons lie symmetrically distributed at the intersections of the giant fullerene half-dome and the more-or-less cylindrical wall which consists purely of hexagons—the whole resulting in a pointed cone-shaped cap. The structure shown actually is half of C_{960} which has a diameter of ca 0.28 nm—very similar to the minimum diameter of the structures observed which have diameters of from 0.30 to 10.0 nm. (Note that the diameter of a symmetric fullerene-n is given fairly accurately by $d = 0.7(n/60)^{1/2}$ nm.) Clearly domes of all shapes, sizes, and symmetries can be constructed by varying the disposition of the pentagons. Indeed various types of nonpentagonal "disclinations" are likely to occur, involving possibly seven- and eight-membered rings, in real macroscopic "defective" carbon cage networks. In addition large scale sheet strain and intersheet forces will all be involved in modulating the observed shapes of the resulting macroparticles.

There is already a significant amount of experimental evidence to suggest that giant fullerenes with hundreds of atoms form. In the study by Rohlfing et al.,[26] in which even-numbered carbon clusters with more than 30 atoms were first observed, clusters with as many as 190 atoms were detected. So and Wilkins[27] observed species with as many as 600 atoms, and, in a recent carbon cluster beam study, Maryuma et al.[21] have detected only even-numbered carbon clusters up to C_{400}. These studies give convincing support to the conjecture that the even-numbered large carbon clusters are indeed giant fullerenes.[14] The question of their general shape is still an open question. It is possible that *gas-phase nucleation* results in some roughly spheroidal shape with some statistically determined range of asymmetry. The pentagon isolation rule[13,28] which proposes that isomers with abutting pentagons are not stable has now been shown to be the decisive criterion for stability of the fullerenes in general. The rule may not apply to *second* order as at this stage there is no evidence that the 12 *isolated* pentagons repel each other further to produce cages in which the pentagons are as far apart as possible—i.e. to produce truly icosahedral giant fullerenes as opposed to quasiicosahedral (distorted) ones.

Thus it is relatively easy to conceive of massive extended *tubular* sp^2 networks which are essentially giant *closed* fullerene tubes (Zeppelenes?), as depicted in Figure 2. In Figure 3, two examples of TEM simulations[23-25] for such giant fullerene end-cap domes of the kind shown in Figure 1 are presented. The ones depicted are pertinant for the present discussion as they clearly show that the fullerene structure does indeed explain the characteristics of the observed TEM images. In this case double layered shells are depicted which have diameters 4 and 5 times that of C_{60}, i.e. 2.8 and 3.5 nm. Depending on the disposition of the pentagons over the cap and the orientation of the cap in the beam, the observed contour may either appear cone-shaped or essentially smoothly hemispherical. In fact the two images shown here are for the same dome at different observation orientations.

Growth

The original spiral growth scheme[7,8] can explain the observation of microparticles and also closure in the case when annealing occurs. If, on the other hand, network growth is very rapid and competes effectively with annealing, then the scheme explains[23] the imperfections in the structures observed originally by Iijima,[18] in particular shell interconnections and shell discontinuities. It should be noted that on the basis of this scheme the occurrence

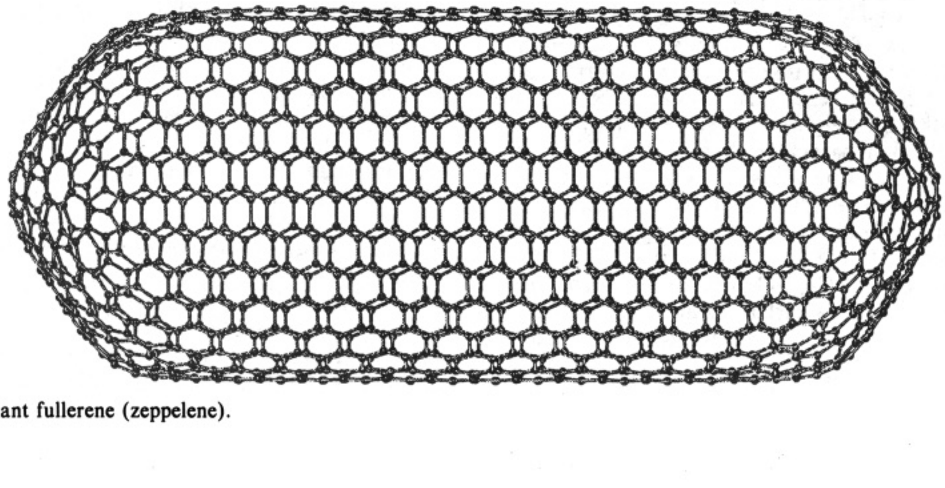

Figure 2. Tubular giant fullerene (zeppelene).

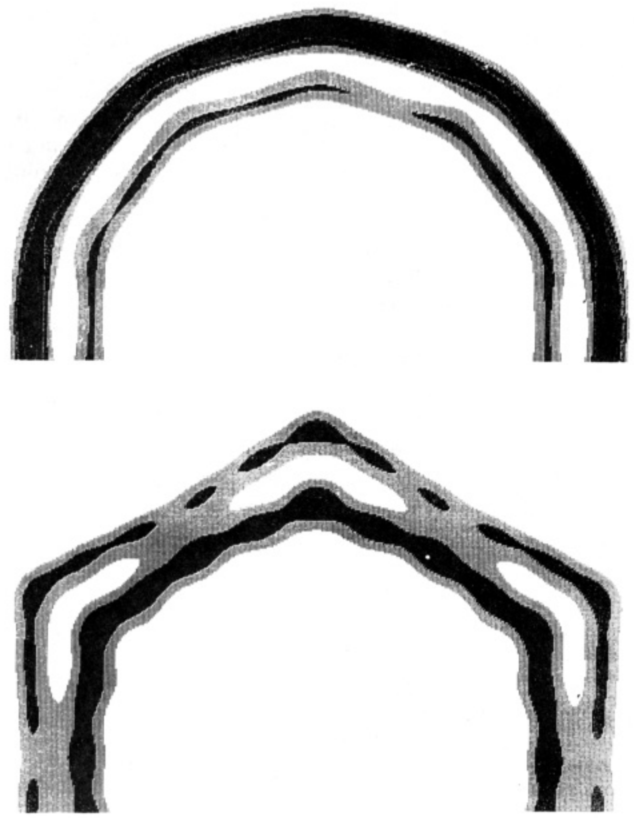

Figure 3. TEM simulations of double layer graphite domes.[23] The difference between these two images is only the disposition of the pentagonal cusps over the surface and the orientation of the cap in the electron beam.

of defects and in particular the intervention of atoms of elements other than carbon—particularly hydrogen should (particularly if involved in small amounts)—also lead to spiral shell structures.

However the new structures[2,4] and somewhat similar ones observed by Iijima originally[18] are overlapped in such a way that some further factor appears to operate. An important characteristic is the general shape of fullerenes and microparticles. The isotropy of gas-phase nucleation should result in roughly (statistically) spheroidal structures, and to some extent this conjecture appears to be born out by the fact that many of the microparticles originally observed by Iijima were indeed spheroidal.[18,19] It is now known however that C_{60} makes up a significant fraction of the soot component in a fullerene arc reactor and that some very large closed species also appear to form. Under such (special?) conditions the nucleation process needs further refinement. A possible synthetic mechanism has been proposed[9,29] to account for the extended carbon networks which were suggested to form during carbon nucleation.[7,8] The mechanism is based on the remarkable observation of Rubin et al.[30] that C_{60} and other fullerenes form spontaneously when large polyyne or cumulene chains/rings polymerize. The proposed concerted cycloaddition process forms an interlocking network leading smoothly to fullerene-60 when C_{30} rings/chains dimerize. In addition to this process, we here propose that a closed fullerene structure may be able to grow further into a larger fullerene by insertion of smaller carbon species directly into a graphite network. Such a process readily explains several observations on the fullerenes and the carbon nanofibers.

The proposal gains support from a series of important observations. Ulmer et al.[31] have seen particularly convincing evidence that fullerenes can indeed grow by addition of smaller carbon fragments. In these experiments C_{60} and C_{70} have been seen to form a whole range of higher fullerenes such as C_{76} and C_{84} when laser irradiated. The most logical explanation of these results is that photodissociation has deflated one fullerene molecule by perhaps the mechanism suggested by O'Brien et al.,[32] and the ejected small carbon fragments have inserted into other fullerenes which have inflated. O'Brien et al.[32] showed that multiphoton fragmentation of fullerene-*n* results in the ejection of even-numbered carbon fragments C_m (i.e. C_2, C_4, C_6, ..., etc.) together with subsequent closure of the network to form fullerene-$(n - m)$. Significantly it was noted that starting from a particular fullerene, for example, fullerene-80, successive fragmentation resulted in fullerene products in which fullerene-70 and fullerene-60 were prominent. This suggests that the pentagon isolation rule[13,28] governs the network infrastructure during the annealing. Indeed the fullerene network may be fluid and network reorganization facile under high energy conditions as Radi et al.[33] have found. Similar studies of fullerene stability at lower energies by Cambell et al.[34] indicate that the fullerenes are, as might be expected, less "fluid" at lower temperatures. Very recently Christian et al.[35] have shown that C_{60} reacts with ^{13}C with zero activation energy to form a labeled C_{61} species which fragments to a C_{60} which is labeled, indicating that carbon atoms can indeed be ingested and dispersed into the cage network as conjectured here.

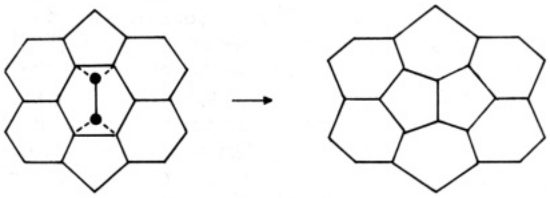

Figure 4. Hypothetical mechanism for insertion of carbon into a segment of a fullerene surface. This process is essentially the reverse of that suggested by O'Brien et al.[32] to account for fullerene photocontraction.

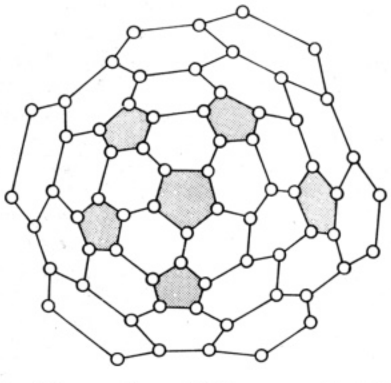

Figure 5. Schlegel diagram for a slightly asymmetric fullerene end cap connected to a helical cylindrical array of hexagonally linked carbon atoms. The pattern in the cylinder wall repeats after 22 atoms are added—two revolutions of the end cap.

A possible insertion mechanism is depicted in Figure 4. This is essentially the reverse of that presented O'Brien et al.[32] Instead of carbon ejection, carbon ingestion is proposed. It is further suggested that the active sites are in the vicinity of pentagons and that the process involves insertion–reorganization processes in which strain is equilibrated by diffusion of the pentagonal cusps. Under anisotropic growth conditions, tube formation is the only likely result due to topological constraints.[24] As pentagon isolation does not appear to operate to second order, it remains to be determined just what electronic, geodesic, and other factors govern the stability of the various isolated-pentagon isotopomers which can exist for larger fullerenes. Stone and Wales have suggested a way in which rearrangements might occur among various isotopomers,[36] and although these processes are Woodward–Hoffman forbidden, at high temperatures the transition states between the various configurations appear to be readily reached.

Iijima has found a most important and interesting property of the carbon atoms in the cylindrical walls of the nanofibers in that they are arrayed in a helical screw relative disposition.[2] One very simple network which indicates how such a helical structure might arise is shown in Figure 5, where the Schlegel diagram for one of the simplest (and smallest) "unsymmetric" (i.e. non-C_{60} type) isolated pentagon fullerene end caps is depicted. Note that although this example is smaller than tubular fullerenes observed by Iijima, which are in general >3-nm diameter, the result obtained is of general validity. In Figure 5, one pentagon is displaced by *one* step from the basic C_{5v} symmetry of a symmetric C_{60}-like half-dome. Addition of hexagons to this six-pentagon configuration results in a cylindrical tube in which the atoms are arrayed in a helix. Addition of two atoms to the wall helix sequence results in a cap which is indistinguishable other than by rotation. If atoms are ingested at the cap and rearrangement occurs so that the new atoms are allowed to knit into the wall, the fluid cap can essentially be considered to move in a screw transformation leaving the wall stationary but growing by insertion of a uniform cylindrical thread of carbon atoms in a symmetrical helical array (Figure 5). This structure offers an intriguing possibility for sequential ingestion of C_4 units to lay down a helical trail of carbon atoms with concommitant pseudocontrarotation of the cap relative to the cylinder wall. It is interesting to note that hydrocarbons which are efficient C_4 precursors are significantly more effective at producing cylindrical carbon particles than other types of hydrocarbon.[29] It may also be noteworthy that the chiral fullerene-76, which has been extracted by Ettl et al.,[37] has the same eccentric Schlegel diagram(s) for its half-shell and a similar disposition of pentagons adjacent the reactive site as in the case of the insertion mechanism depicted in Figure 4.

Clearly once one layer has been formed it is possible that a second layer might form epitaxially to cover an existing surface. In the original mechanism, this was thought unlikely as it was assumed that it would be difficult for a new layer to form in the gas phase. The necessity for some sort of chemically bonded keying-in (or -on) to an already closed fullerene surface seemed unlikely, and van der Waals forces do not seem adequate especially in the gas phase at high temperatures. The realization that direct insertion is feasible however suggests that this may be a possible "key" process. On the other hand, whether "perfect" isolated nested structures[23-25] can form to any significant extent, either directly or by delayed annealing of some initially imperfect concentric spiral shell structure of the kind observed in earlier study by Iijima,[18] has still to be ascertained. However the more recently observed nanofiber structures do appear to have some of the same basic characteristics. As such objects appear to grow from a surface, it may be that the keying-in of secondary layers occurs at contact points between a closed or semiclosed structure and the surface upon which it is deposited. Certainly tubular growth only is likely to occur from a surface deposited nucleus.[24]

A further particularly interesting possibility is that an *outer* layer may grow by insertion independently, leaving behind the inner surface intact. As the inner surface was the original template for the secondary growing layer, the latter may retain some residual memory (shape) of the underlying template structure, especially if further growth is fairly limited. Such a secondary growth/extension phase would explain why compartments are detected by Endo[4] and Iijima.[2,18,22] Furthermore there appears to be a relationship between the secondary extended layer and the underlying primary surface suggestive of a template memory effect in these objects.[4,18]

Discussion

Some aspects of the fullerene discovery have been discussed and seen to shed light on the recent observations on nanofibers and fullerene growth and structure. The growth mechanism would explain why closed shell structures appear so prevalent in some cluster beam experiments, particularly under conditions where annealing appears to be important and nucleation prolonged. Insertion into a fullerene end cap accompanied by some "fluidlike" rearrangement (rather like a reverse musical chairs mechanism) would neatly explain many aspects of carbon nanofiber structure, in particular their apparent unidirectional growth. The fascinating observation by O'Brien et al.[32] that C_n species where $n > 70$ can deflate to C_{70} and then on to C_{60} bears adequate witness to the fact that complex rearrangements of the carbon network are facile—at least at high temperatures. There is thus every reason to expect that similar rearrangements may occur when the reverse process—inflation—occurs. The nanofibers appear to grow out from a surface, and thus anisotropic growth presumably under inhomogeneous thermal conditions appears to have taken place. Under these conditions, it seems quite reasonable that growth would occur from one side leading to the advance of a semifluid cap which would leave behind a cylindrical graphite wall. In the case of anisotropic growth, anything other than tube formation is not likely to be uniformly self-propogating.[24]

Under certain conditions—which the observation of multiple walls suggests are common—ingestion of carbon at the end cap and the concommitant tube extension appears to slow down. Further epitaxial deposition then takes place, and secondary (and higher order) layer growth takes place over previous fiber surfaces. The surface layer should preclude further growth of underlying layers, and nested configurations are to be expected[23-25] and appear to be observed.[2,4]

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