

High-resolution Electron Microscopy Studies of a Microporous Carbon produced by Arc-evaporation

Peter J. F. Harris

Chemical Crystallography Laboratory, University of Oxford, 9 Parks Road, Oxford, UK OX1 3PD

Shik Chi Tsang, John B. Claridge and Malcolm L. H. Green

Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, UK OX1 3QR

The soot produced as a byproduct of fullerene synthesis by arc-evaporation consists of a microporous carbon with a surface area, after activation with carbon dioxide, of *ca.* 700 m² g⁻¹. Here, we investigate the structure of this material, and its appearance after electron irradiation and high-temperature heat treatment, using high-resolution electron microscopy. We show that the heat treatment transforms the new carbon into a structure containing large, tube-like pores, rather than into polycrystalline graphite. This suggests that the arc-evaporated carbon may have a novel, fullerene-related microstructure, and that it may be the precursor for nanotube formation.

The discovery that C₆₀ and other fullerenes could be extracted from the carbon soot produced by arc-evaporation of graphite rods¹ has stimulated enormous interest. Naturally, most of this interest has focused on the fullerenes themselves rather than on the residual soot which remains following fullerene removal. Nevertheless, there are good reasons to believe that this residual material also has a novel microstructure which may be of considerable theoretical and practical interest. In a recent study² we investigated the properties of the soot following removal of fullerenes and 'activation' in carbon dioxide. We found that the material had a very high internal surface area (*ca.* 700 m² g⁻¹), and that it displayed molecular sieving properties indicative of a microporous structure with most of the pores ≤ 5 Å in diameter. High-resolution electron microscopy (HREM) confirmed that the structure was highly microporous, with an appearance quite similar to that of some conventional high-surface-area carbons.

Here, we describe a more detailed programme of studies of the arc-evaporated soot using HREM. We compare the properties of the soot with those of a high-surface-area carbon prepared by pyrolysis of Saran resin, a poly(vinylidene chloride)/poly(vinyl chloride) copolymer. In this way we aim to determine how the fullerene-related soot differs from conventional microporous carbon.

Experimental

Preparation of Arc-evaporated Soot

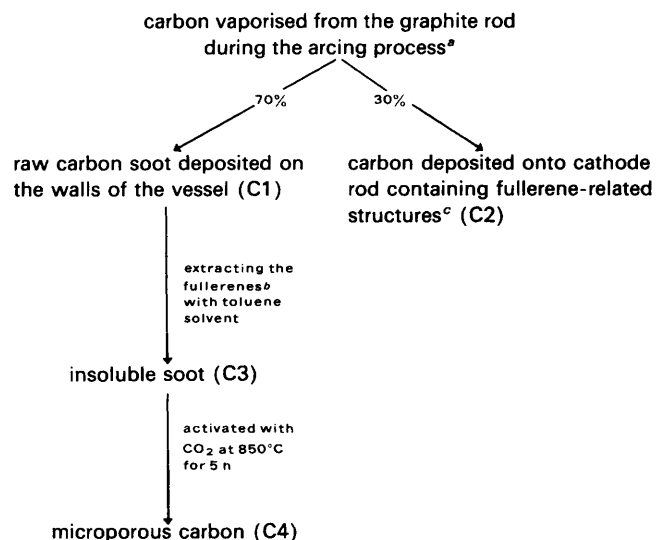
Arc-evaporation of graphite rods was carried out in the standard way for C₆₀ production. Thus, electrolytic grade rods were arced in 150 Torr helium using a dc voltage of 32 V and a current of 180–200 A. Under these conditions *ca.* 70% of the vaporised carbon deposited onto the walls of the evaporation vessel, while *ca.* 30% 'distilled' onto the cathodic rod, as shown in Scheme 1. The soot which formed on the walls of the vessel (C1) was carefully collected and the soluble fullerenes were extracted with toluene for three days in a Soxhlet apparatus, after which the solvent was removed under reduced pressure. The residual insoluble soot, C3, was then dried and activated by treatment in a stream of carbon dioxide, with a flow rate of 20 ml min⁻¹, at 850 °C for *ca.* 5 h. Under these conditions the reaction C + CO₂ → 2CO occurs and after the 5 h period a weight loss of *ca.* 15% was observed. The final product was a microporous carbon which we designate C4.

Preparation of Saran Char

The starting material was Saran 416 powder, a copolymer containing *ca.* 90% poly(vinylidene chloride) (PVDC) and 10% poly(vinyl chloride) (PVC), with a melting point of 445 K. 1 g of the powder was first heated to 438 K under nitrogen and held at this temperature for 68 h. The sample was then further heated to 933 K under nitrogen at a rate of 1 K min⁻¹ and was held at this temperature for 12 h, before being cooled to room temperature under nitrogen. The apparent surface area of the resulting carbon measured by BET (N₂) was 655 m² g⁻¹.

High-temperature Heat Treatment

The arc-evaporated carbon C4 and the Saran char were both subjected to high-temperature heat treatments under vacuum in a positive-hearth electron gun (4 kV, 0.4 A) for periods of *ca.* 4 h. Although an exact measure of temperature was not



^a Arc provided by a dc supply at *ca.* 200 A and 32 V. ^b The extracted fullerenes (3–5%) are C₈₀, C₇₀ and higher fractions. ^c The fullerene-related structures include nanotubules (buckytubes) that are closed at both ends and some nanoparticles.

Scheme 1

made, samples typically reach temperatures in the region of 2500–3500 K in this apparatus.

High-resolution Electron Microscopy

Specimens were prepared for electron microscopy by grinding them gently in a pestle and mortar and dusting the powder directly onto holey carbon films. The microscopes employed were a JEOL 2000FX instrument with a maximum accelerating voltage of 200 kV and a JEOL 4000FX instrument with a maximum accelerating voltage of 400 kV. Only thin regions which extended over a hole in the support film were imaged.

In addition to imaging the samples, we carried out a series of electron irradiation experiments on both the C4 carbon and the Saran carbon. Ugarte has demonstrated^{3,4} that electron irradiation can transform nanotube-containing soot into quasi-spherical concentric fullerene particles ('carbon onions'), and we have shown² that C4 can also be transformed into onions in this way. The aim of the present experiments was to compare the behaviour of a conventional carbon during electron irradiation with that of the arc-evaporated carbon. The irradiation experiments involved removing the microscope's condenser aperture and focusing the beam on a small area of sample for periods of up to 2 h. A range of accelerating voltages were used for the irradiation, from 200 to 400 kV.

Results

Examination of Freshly Prepared Carbons

Plate 1 shows a typical high-resolution micrograph of the microporous carbon C4. It can be seen that the structure consists mainly of randomly curved layers enclosing micropores in the sub-nanometre range. In some areas, spiral arrangements of layers were present, as indicated in Plate 1, but the interlayer spacings in these spiral structures were *ca.* 5–6 Å, *i.e.* considerably larger than the graphite *c* distance of 3.4 Å. Small graphitic regions were sometimes seen, and occasionally nanoparticles similar to those observed in the cathodic soot were observed,⁵ but the great majority of the material displayed no obvious crystalline order.

The carbon prepared from Saran was somewhat similar in appearance to the C4 carbon, as shown in Plate 2, although the carbon layers appeared to be somewhat more tightly packed, and no obvious spiral structures were seen.

Electron Irradiation

When the C4 carbon was irradiated with an intense electron beam in the 2000FX instrument, using an accelerating voltage of 200 kV, a transformation to quasi-spherical concentric fullerene particles was observed after a period of 30–40 min. Surprisingly, irradiation at the same accelerating voltage in the 4000FX instrument did not produce a similar transformation even after periods of greater than 1 h. Irradiation in this instrument at higher voltages (300 and 400 kV) similarly failed to produce a complete transformation into onions, although a rounding of the overall morphology was observed. This difference between the behaviour of C4 under irradiation in the two microscopes is not yet understood, but two possible reasons suggest themselves. First, the beam current in the 4000FX was probably lower than in the 2000FX. A direct measure of beam current was not possible because the intensities employed were higher than the maximum that could be recorded by the microscopes. Also, the smallest spot size obtainable on the 4000FX appeared somewhat larger than that obtained on the other microscope. In either case, these experiments indicate that beam current

may be more important than accelerating voltage in inducing onion formation.

A high-resolution image of a region of C4 which has been completely converted into spheroidal onion particles is shown in Plate 3. It can be seen that the range of particle sizes is rather narrow: the smallest onion observed consisted of three concentric layers (approximate outer diameter 21 Å) and the largest of 12 layers (approximate outer diameter 82 Å). Ugarte observed a much broader range of sizes in irradiated nanotubes/nanoparticles. In general, the onions appeared to be approximately spheroidal, although sometimes they were observed to pass through a faceted configuration. Plate 4(a) shows a nine-shell particle with a circular outline, while Plate 4(b) shows the same particle a short time later exhibiting slight faceting. This phenomenon of momentary faceting was also reported by Ugarte.⁴ As pointed out by a number of workers, it is surprising that more faceting is not observed. If the onions are assumed to consist of concentric fullerenes, then the giant fullerenes which make up the outer shells would be expected to experience considerable strain when forced into an approximately spherical shape. More work is needed to understand why the onions are so remarkably spherical.

Electron irradiation of the Saran carbon was also carried out. Evolution into carbon onions also occurred here, although considerably longer irradiation times were needed than for the C4 carbon (this probably explains why onion formation was not observed in our previous study² when we irradiated a microporous carbon derived from coconut shell). Plate 5 shows a Saran sample following irradiation for *ca.* 100 min at 200 kV in the 2000FX instrument. Again, the irradiated region appears to have been almost completely converted into spheroidal onion particles, and there is a slightly wider range of particle sizes than for the C4 carbon. Note that this is the first demonstration of onion formation by the irradiation of a conventional (as opposed to arc-evaporated) carbon.

Heat-treated Carbons

High-temperature heat treatment of the arc-evaporated carbon C4 produced a structure apparently made up of large pores which were often extended in shape, resembling single-layer nanotubes, as can be seen in the micrograph shown in Plate 6. Like nanotubes, the extended pores were almost invariably closed, and exhibited a variety of capping morphologies. In some cases features were observed which are thought to be indicative of the presence of seven-membered carbon rings;^{6,7} an example is arrowed in Plate 6. In most cases the extended pores were bounded by single carbon layers, although multilayer structures were also present, as shown in Plate 7. Other structures were also seen, which appeared to be random in shape rather than tube-like, often exhibiting quite sharp faceting. We note that de Heer and Ugarte⁸ have found that raw fullerene soot (C1) can also be transformed into nanoparticles and nanotubes by high-temperature heat treatment.

A similar heat treatment of the Saran char produced a quite different structure, as shown in Plate 8. Here, the microporosity of the original material has disappeared, and has been replaced by a polycrystalline structure made up of conjoined graphitic layer groups. This kind of structure is typical of 'non-graphitising' carbons following high-temperature heating.⁹

Discussion

In this study we have attempted to distinguish between the microporous carbon produced by arc-evaporation, C4, and a

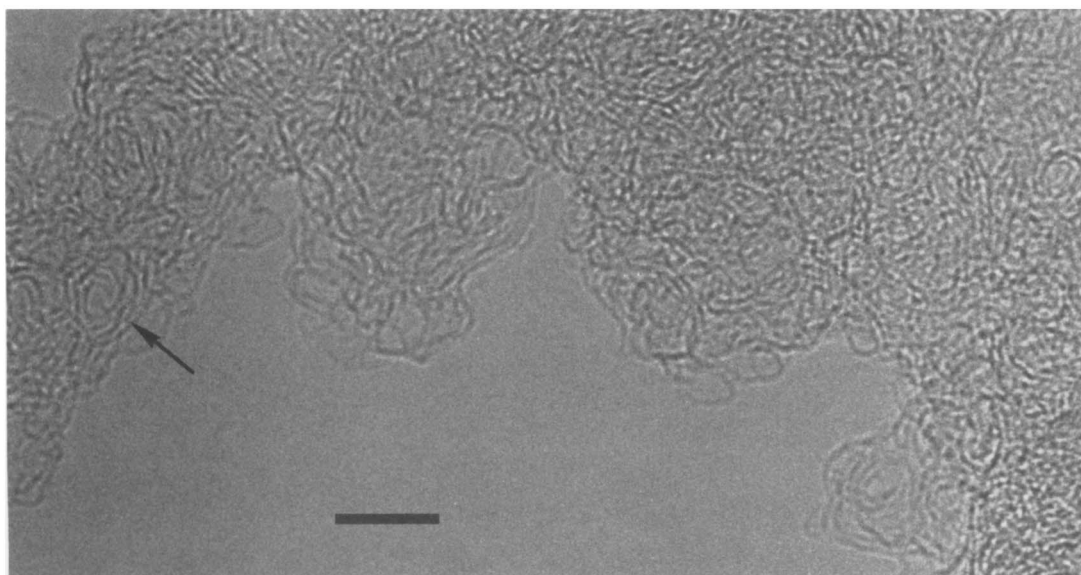


Plate 1 High-resolution electron micrograph of the microporous carbon C4. Arrow shows area with apparently spiral structure. The scale bar in this and all other figures is 50 Å.

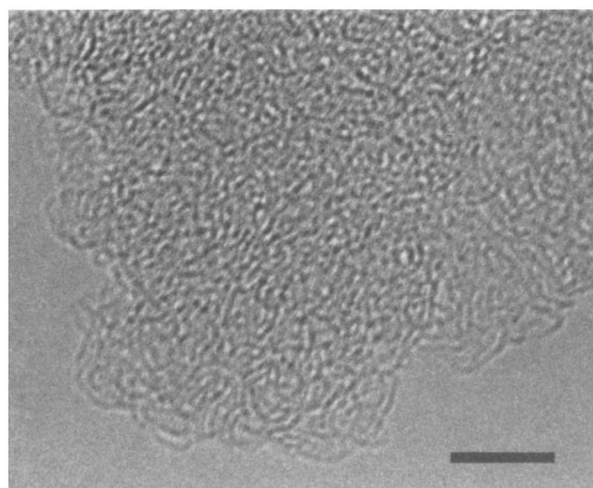


Plate 2 Micrograph of the Saran-derived microporous carbon

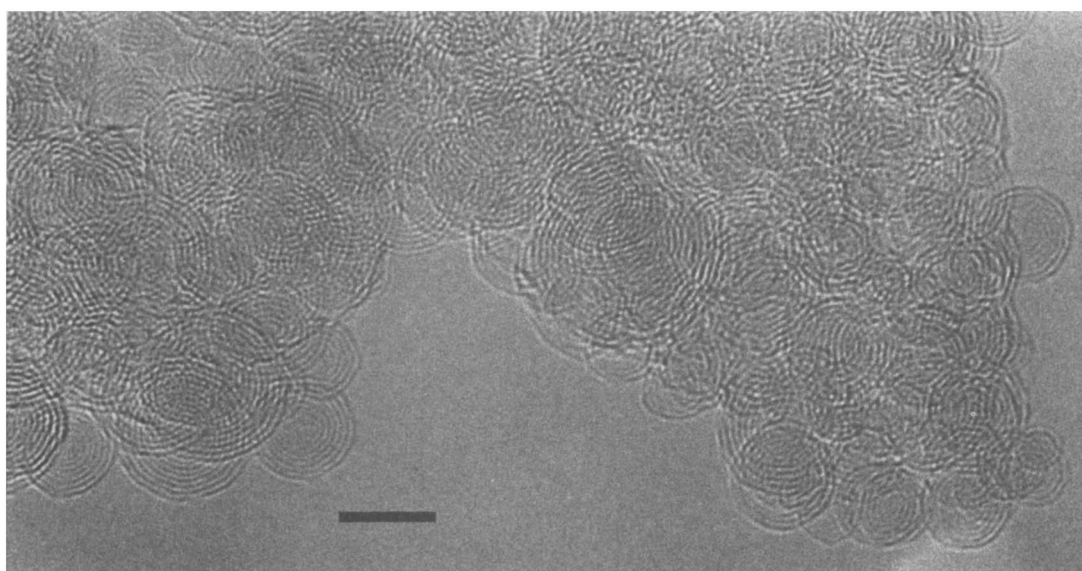


Plate 3 Micrograph of C4 carbon following intense electron irradiation at 200 kV for *ca.* 30 min, showing region completely transformed into quasi-spherical concentric fullerene particles (carbon onions)

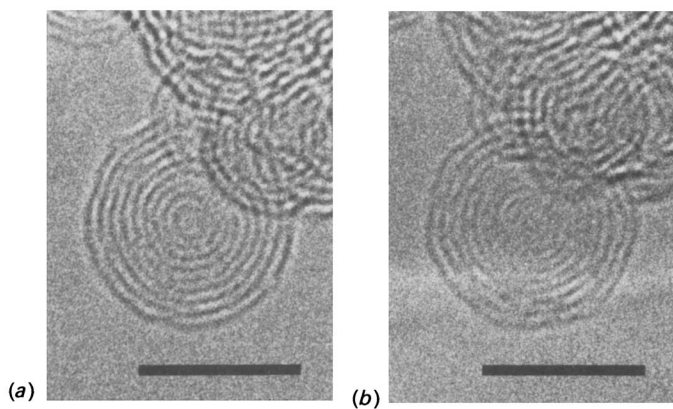


Plate 4 Nine-shell carbon onion particle in irradiated C4 sample: (a) image showing circular profile, (b) image displaying slight faceting

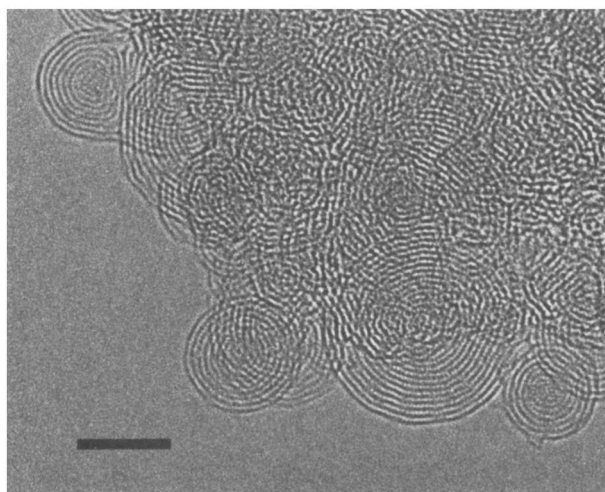


Plate 5 Carbon onions formed by electron irradiation of Saranderived carbon

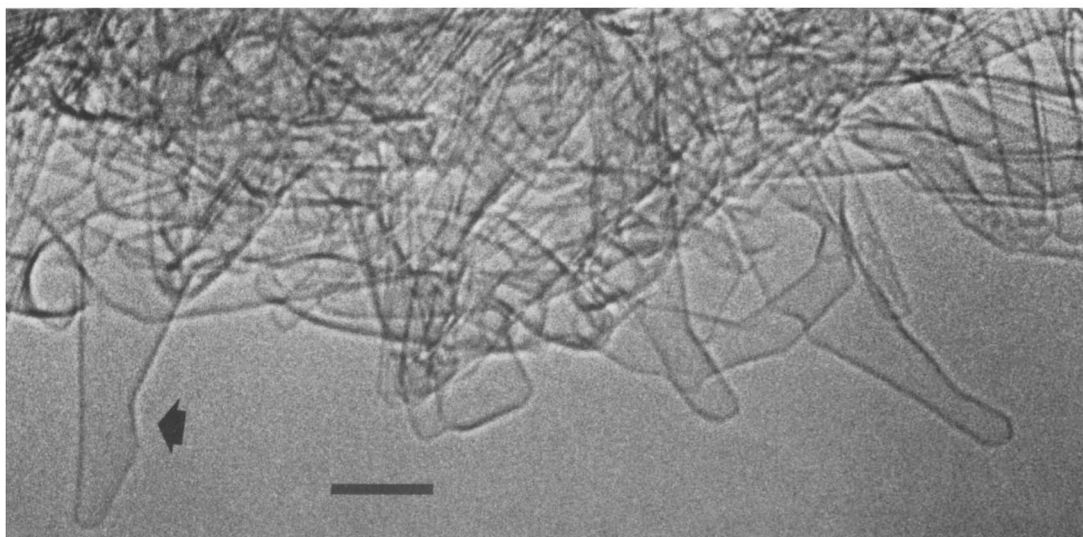


Plate 6 Micrograph of C4 carbon heated to 2500–3000 K for 4 h using a positive-hearth electron gun, showing development of large tube-like pores. Arrow indicates morphological feature indicative of the presence of heptagonal rings.⁷

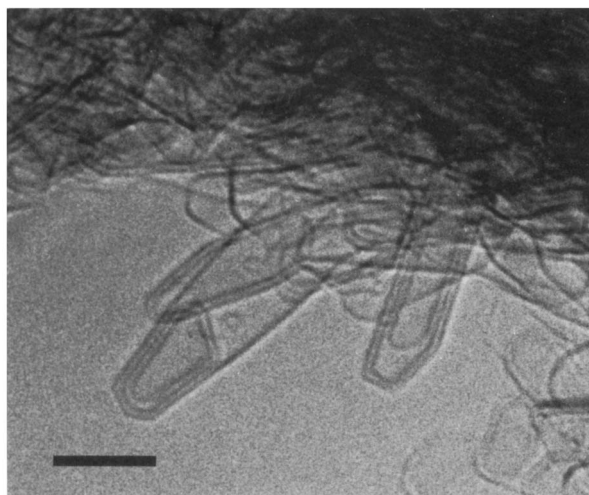


Plate 7 Multilayer tube-like structures in heat-treated C4 carbon _n

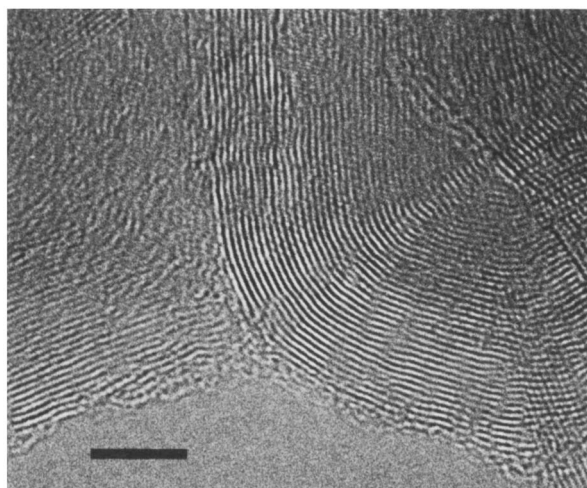


Plate 8 Saran carbon following heat-treatment with electron gun, showing extensive development of graphitic structure

conventional microporous carbon derived from Saran polymer, by using HREM. We first examined both materials in their fresh state and found them to be very similar in appearance. We then carried out a series of electron irradiation experiments on both the C4 carbon and the Saran carbon and found that in both cases a transformation to concentric fullerene particles was observed. This shows that the occurrence of such a transformation does not imply that the original carbon must have a fullerene-related microstructure, as we suggested in our earlier paper.² However, note that the transformation to 'onions' was considerably easier for the C4 carbon than for the Saran carbon, suggesting that it has a more fluid structure.

High-temperature heat treatments were then carried out on both materials, and here a very striking difference in behaviour was observed. In the case of the Saran carbon, the heat treatment resulted in the formation of polygonised and bent layer groups similar to those observed many years ago in studies of 'non-graphitising' carbons.⁹ However, high-temperature heat treatment of the C4 carbon resulted in a quite different structure apparently made up of large pores, often with extended, tube-like shapes. These tube-like pores were invariably capped, indicating the presence of pentagonal rings, and, as noted above, often displayed morphological features which have been interpreted as resulting from heptagonal rings.^{6,7} We therefore believe that the original structure of C4 contains both pentagons and heptagons distributed randomly throughout a hexagonal network, producing continuous curvature, as shown in Fig. 1. This structure resembles the 'random schwarzite' structure proposed by Townsend *et al.*,¹⁰ although with many fewer seven-membered rings. Also, we believe that C4 consists of relatively small fragments, rather than the extensive structure envisaged by Townsend *et al.* Other workers have put forward similar models of 'fullerene soot' to the one we have proposed,^{11,12} although they have tended to emphasise the importance of spiral structures in the soot. There is some evidence that spiral structures are present in C4 (see Plate 1), but the majority of the material does not seem to have this form.

We believe that it is quite feasible that a structure such as the one shown in Fig. 1 could form in a carbon arc. According to the 'pentagon road' theory of fullerene assembly,¹³ the formation of isolated pentagonal rings is energetically favoured during condensation as this leads to the minimisation of dangling bonds. In C₆₀, 12 isolated five-membered rings are distributed symmetrically to produce the closed, icosahedral structure. However, if pentagons were to occur in the 'wrong' positions then closure would be much

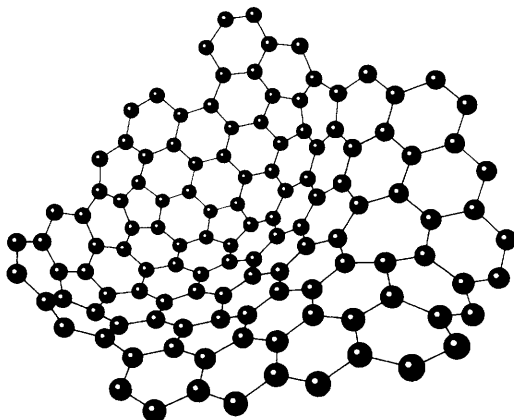


Fig. 1 Illustration of our proposed structure for C4 carbon. The fragment shown has 45 hexagons, four pentagons and one heptagon.

less likely, and a randomly curved structure might develop. Kroto and McKay considered a similar growth mechanism,¹⁴ but assumed that pentagons would stack epitaxially one above the other, leading to spiral shell structures. As noted above, the structure of C4 does not appear to be dominated by spiral structures.

The observation that C4 can be transformed into nanotube-like structures by high-temperature heat treatment suggests that it may be the precursor for the production of carbon nanotubes. One could therefore propose the following model for nanotube formation. In the initial stages of arc-evaporation, a C4-like material (plus fullerenes) would condense onto the cathode, and the condensed material would then experience extremely high temperatures as the arcing process continued, resulting in the formation first of single-layer, nanotube-like structures and then of multilayer nanotubes. This contrasts with previous models of nanotube formation, which have envisaged a direct vapour-condensation process. One could also speculate that the spiral structures observed in C4 might be the precursors for the nanoparticles, which are also invariably present in cathodic soot.⁵

Recent work by Lin *et al.*¹⁵ has produced very interesting results which appear to confirm our model of nanotube growth. They carried out arc-evaporation employing a composite anode, the centre of which consisted of a copper rod. The central region of the resulting cathodic deposit was found to contain many single-layer structures similar to those reported here, while the outer region consisted largely of multilayer tubes. They speculate that this could be a result of a change in the temperature distribution on the electrode surfaces due to the presence of copper in the anode. This would be consistent with the model of nanotube growth presented here, since in their experiment the central region of the cathodic deposit would presumably experience a lower temperature, so that the C4 material would be transformed only to single-layer structures, while the outer region would experience temperatures similar to those produced in a normal arc, resulting in multilayer structures.

A comment should be made here on the reactivity measurements described in our previous paper.² We reported there that the carbon C4 was less reactive towards oxidation with carbon dioxide than conventional microporous carbon. We now believe that these measurements may be misleading owing to the presence of potassium in the conventional carbons, leading to enhanced reactivity. Experiments are in progress to establish the true reactivity of C4 in comparison with conventional microporous carbon.

Finally we note that the new arc-evaporated microporous carbon may have many novel and useful characteristics in addition to those we have already described. Thus its electronic and optical properties, for example, may be worthy of further study.

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