Hollow structures with bilayer graphene walls

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Abstract
The formation of three-dimensional shell-like structures with bilayer graphene walls is described. The structures are produced by the passage of an electric current through graphite in an arc-discharge apparatus. High resolution transmission electron microscopy is used to characterize the carbon, and provides evidence that the structures are three-dimensional rather than flat. A striking feature of the material is that it contains bilayer nanotubes seamlessly joined to larger shell-like regions. The possible growth mechanism of the carbon is discussed, and potential applications considered.

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1. Introduction

Experiments with a graphite arc have proved to be extremely fruitful for carbon research. In 1960, Roger Bacon used a DC arc to produce graphite whiskers, scroll-like graphite fibres with outstanding mechanical properties [1,2]. This proved to be a key event in the development of carbon fibres. Thirty years later, Krätschmer and Huffman and their co-workers achieved the first bulk synthesis of C_{60} using an arc-evaporator [3], a development that gave a huge boost to fullerene research. Shortly afterwards Iijima [4] produced highly perfect multiwalled carbon nanotubes using arc-evaporation, and in 1993 Iijima and Ichihashi [5] and Bethune and co-workers [6] showed that single-walled nanotubes could also be made in this way. Recently, yet another kind of carbon has been discovered in graphite samples which have been subjected to arc-discharge [7,8]. This new carbon apparently consists of hollow graphitic shells bounded by curved and faceted planes, typically made up of two graphene layers. The curvature and faceting appears to be due to the presence of a small number of pentagons and other non-hexagonal rings distributed in a hexagonal graphene network. The hollow structures, which can be several 100s of nm in size, are frequently decorated with nano-scale

carbon particles, or short nanotubes; in some cases, nanotubes are found to be seamlessly joined to the thin shells.

In this paper, the synthesis of these novel carbon structures, and their characterisation by high resolution transmission electron microscopy, is described. Evidence that the structures are three-dimensional rather than flat is presented, and the possible formation mechanism of the structures is considered, although many aspects of this remain poorly understood. In particular is not clear why the great majority of the hollow particles have bilayer, rather than monolayer or multi-layer walls. It is suggested that this may be related to the edge structure of the original graphite. The relationship between the new structures described in this paper and rather similar ones reported in 2009 by Jia *et al.* [9] and by Huang and colleagues [10] is discussed. In these latter papers, a structural transformation of graphite similar to that reported here was produced by the *in situ* heating of graphite "nanoribbons" inside a TEM. This was explained in terms of sublimation and edge reconstruction of flat graphene, but may actually have involved a transformation from flat graphite to hollow structures, as described in the present work.

The new carbon materials may have useful applications in a number of areas. With their extremely large surface-to-volume ratios they could be useful as hydrogen storage materials or in catalysis. They could also be of value in electrical devices such as supercapacitors or lithium ion batteries, where their structural stability might give them advantages over materials assembled from graphene flakes by solution or other methods.

2. Experimental Methods

The graphene material described in this paper was prepared in a commercial arc-evaporator, a Quorum Q150T ES, which is normally used for carbon-coating specimens for electron microscopy. In this unit the electrodes are 3 mm graphite rods, one of which is thinned to a diameter of approximately 1.4 mm and held in contact with the other electrode with a spring mechanism. The chamber is pumped by a turbomolecular pump to a pressure of approximately

3 x 10^{-4} mbar. Before carrying out the "evaporation", the rods are out-gassed by passing a current of about 30A for 1 minute. For evaporation, a current of 75A is passed for 3 s.

Following evaporation, the thinner carbon rod was found to have slightly shortened, and a small deposit was formed in the area where the two rods made contact, as shown in Fig. 1. This was collected and prepared for TEM by grinding in an agate mortar under isopropanol, mixing in an ultrasonic bath and depositing onto lacey carbon TEM grids. The microscope used was a JEOL 2010, with a point resolution of 0.19 nm, operated at an accelerating voltage of 200kV. Images were recorded digitally using a Gatan Orius 200 camera. Samples from the fresh graphite rods were also imaged, for comparison with the carbon collected after arcing.

3. Results

A typical image of material from the fresh graphite rod is shown in Fig. 2(a). As expected, this consists mainly of flat crystallites, ranging from a few 100 nm to about 5 μm in size, containing up to 100 layers. The crystallites were often folded and buckled, and were covered with small amounts of finely-divided material. However, nanotubes or other fullerene-related structures were not seen in the fresh graphite.

The carbon collected from the graphite rods following arcing contained some "normal" graphite, but this was accompanied by many regions which had a very different appearance. One of these areas is shown in Fig. 2(b). Here, the outline of the structure is much more irregular than in the fresh graphite, with many curved and unusually-shaped features, including re-entrant structures. The material is decorated with numerous short nanotubes or nanoparticles. The proportion of carbon in the arc-treated samples which had this altered structure is difficult to estimate with any accuracy, but typically it appeared that about 50% had been transformed in this way.

Micrographs recorded at higher magnifications showed that the thin structures consisted largely of bilayer graphene. An example is shown in Fig. 3. The

bilayer spacing, determined from this and other images, was generally somewhat larger than the interplanar spacing for graphite, being typically around 0.4 nm. The possible cause of the preferential formation of bilayer graphene is discussed below. Single-layer graphene was only rarely seen; regions with 3 or more layers were more common. The nanotubes and nanoparticles which were supported on the larger structures were also generally bilayer, although nanoparticles with many layers were sometimes seen.

Several features of the unusual structures observed in the arc-treated carbon suggest that the material consists of three-dimensional, hollow structures rather than flat bilayer graphene. One notable observation is that small nanoparticles or nanotubes are sometimes seen apparently *inside* larger structures. Figure 4 shows an example, where a small, single-walled nanotube appears to be encapsulated in a bilayer structure. Another striking feature of the graphitic material was that nanotubes were often observed to be joined to the larger regions. Several examples of this are shown in at low magnification in Fig. 5 (a). The tubes were generally 3 – 6 nm in diameter. Higher resolution images, such as that in Fig. 5 (b), showed that the nanotubes were almost invariably bilayer, and were seamlessly joined to the larger structures. This provides further evidence that the large bilayer structures are three-dimensional rather than flat, since it is difficult to envisage a way in which nanotubes, with their circular cross-section, could be connected to flat, few layer, graphene without being seriously distorted, at least in the vicinity of the junction.

The exact nature of the junctions between the tubes and the larger shell-like regions is not known at present. A number of authors have analysed the possible ways in which a nanotube could be joined to a graphene sheet (e.g. [11-13]), but these have all involved tubes bonded to flat graphene planes. In the present case, the nanotubes seem to be joined to cone-shaped regions. It is possible that the junctions may be similar to those observed in certain nanotube tips where a short cylindrical region joins a conical structure [14]. Such structures involve a -60° disclination, believed to be due to the presence

of a heptagonal ring, but more work is needed to establish the precise structure of these connections.

4. Discussion

A striking transformation in the structure of graphite as a result of the passage of an electric current in an arc-discharge apparatus has been described. This apparently involves the formation of three-dimensional shell-like structures bounded by very thin walls, which in most cases consist of bilayer graphene. As mentioned in the previous section, there any several reasons for believing that these new structures are three-dimensional and hollow rather than flat. These include the observation that small nanoparticles or nanotubes are sometimes seen encapsulated inside larger structures, and that nanotubes are often found to be seamlessly joined to the thin shells.

The mechanism of the transformation is not known at present, but it is possible that the key to understanding the process may lie in the edge structure of graphite. It is well established that graphite planes often have "closed" edges, so that the layers resemble folded sheets [15-19], as illustrated in Fig. 6 (a). The transformations reported in this paper may simply involve an "opening" of the layers, as shown schematically in Fig. 6 (b). Such a process might be initiated by the nucleation of pentagonal rings at the closed edges: it is clear from the presence of nanotube-like structures in the carbon that pentagons are present. It also seems clear that the electric current passing through the carbon, rather than simply the high temperature, is responsible for the transformation. However, further work is needed to gain a more detailed understanding of the process.

Transformations rather similar to those described here were reported in two studies published in 2009 by Jia *et al.* and Huang *et al.* [9,10]. These studies involved *in situ* Joule heating of graphite nanoribbons inside a TEM, which resulted in the formation of complex edge structures, sometimes with short nanotubes attached to larger areas. In both papers the authors drew a different conclusion about the nature of the transformation to that given here: the process was discussed in terms of sublimation and edge reconstruction of

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flat graphene. It seems more likely that they were actually seeing a transformation from flat graphite to hollow structures, as described in the present work, rather than sublimation. However, there was one important difference between the structures seen in the Jia and Huang studies and the ones reported here. The hollow structures described in the present study were almost invariably bounded by bilayer graphene walls, while the structures in the 2009 work were virtually all single layer. This may reflect differences in the precursor graphites used for these experiments. In the present work it has been suggested that the precursor graphite had edges in which two adjacent bilayers were joined, as shown in Fig. 6 (a). It may be that in the precursor graphite used by Jia and Huang, only adjacent monolayers were joined. This raises interesting questions about the edge structures of graphites, an area that has not yet been studied in detail.

The material reported in this paper could be described as "three-dimensional graphene". In recent years a number of groups have described the production of three-dimensional structures constructed from graphene, or graphene oxide, but these materials differ in significant ways from the structures reported here. In most cases the methods used to assemble the graphene flakes have involved suspending them in a solvent, using chemical methods to link them together and then removing the solvent in a controlled way [20-23], although a chemical vapour deposition method has also been reported [24]. These techniques produce porous graphene structures, with pore sizes typically of the order of a few 10s of μm. In these structures the graphene fragments are held together by weak Van der Waals type forces, suggesting they would possess a relatively low rigidity, and that the pore structure would be prone to collapse. The new carbon structures described in the present paper differ from these materials in that the porosity is on a much smaller scale, and results from the presence of a small number of pentagons, plus a few other non-hexagonal rings, distributed throughout the graphene network. The "three-dimensionality" is thus a consequence of the chemical bonding configuration in the structure, producing far greater strength and resilience than in the materials produced by assembling graphene flakes.

Concerning potential applications of the three-dimensional graphene structures, these could lie in a number of areas. One possibility might be hydrogen storage, since forms of carbon rather similar to those described here have been shown to have good H_2 storage capabilities. Thus, Orimo *et al.* reported in 1999 that "nanostructured graphite" prepared by mechanical milling of synthetic graphite can have high H_2 uptakes [25]. Carbon nanohorns have also been shown to have potentially useful H_2 storage properties [26]. Theoreticians have suggested that "pillared graphene", a three-dimensional network constructed from graphene and short nanotubes, could adsorb 6% of its weight in hydrogen at room temperature and pressure [27]. Although the present material is a disordered rather than an ordered network, its H_2 storage characteristics might be similar to those of "pillared graphene".

The new structures may also have applications in electrical devices. A number of studies have demonstrated that various forms of modified graphene can be used to produce supercapacitors with high specific energy densities [e.g. 28 - 30]. The graphenes used in these studies are typically produced by exfoliating graphite [28] or by chemical vapour deposition [30]. Although these materials initially have the high surface areas required for supercapacitors, it is not clear that they would retain these surface areas under operating conditions: the flat graphene flakes would have a tendency to clump together. In contrast, the curved and faceted shells described in the present paper would be much more likely to retain their surface area. As well as supercapacitors, there has been great interest in using graphene in the anodes of lithium ion batteries [31]. The large internal volume, stability and high conductivity of the structures described here suggest they might also be useful in this area.

Finally it is interesting to reflect that, although the products of carbon arcs have been studied intensively since Bacon's work in 1960, and carbon arcs themselves have been used since the early 19th century, it appears that the kind of structures described in this paper were not observed before 2009. As Peter Thrower perhaps knows better than anyone, carbon is a material which continues to produce surprises.

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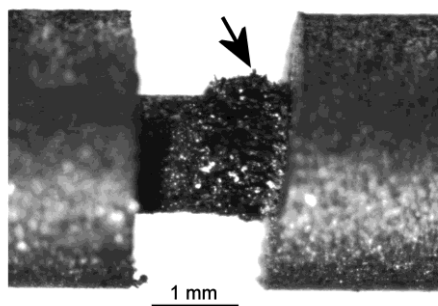
Figures

Figure 1   Photograph of graphite rods following passage of current in arc-evaporator. Arrow indicates deposit containing unusual graphene material.
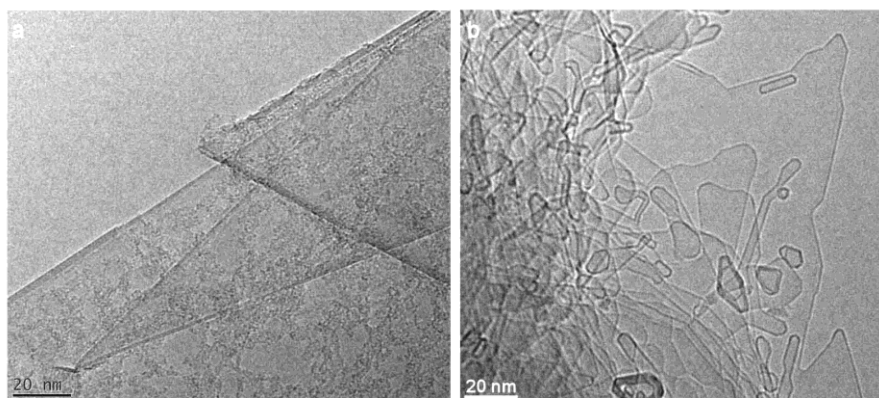

Fig. 2

Figure 2   (a) Transmission electron micrograph of carbon from fresh graphite rod. (b) Micrograph at same magnification showing transformation in structure following arc-discharge.
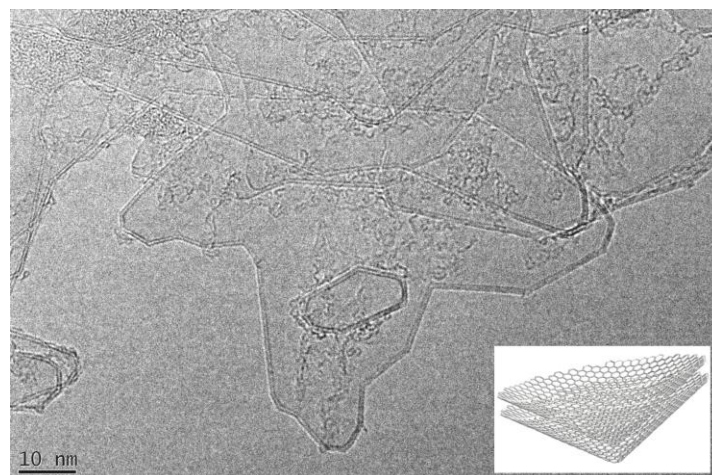
Figure 3   Typical structure of carbon following arc-discharge. Almost all
                the material in this image is bilayer.
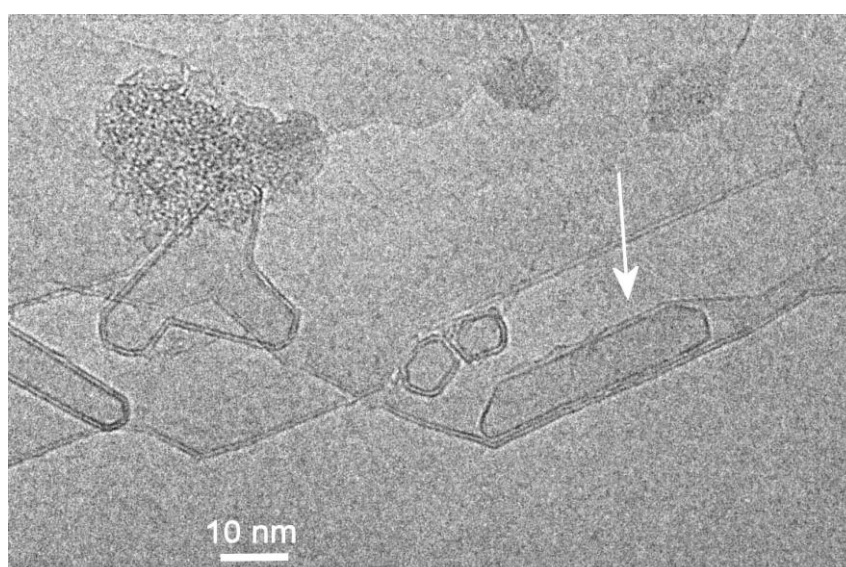

Figure 4   Hollow graphene structure with single-walled nanotube
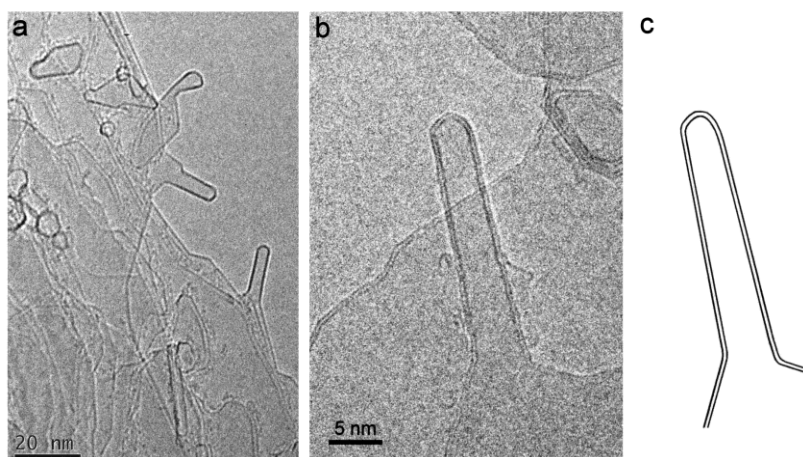   apparently encapsulated inside (arrowed).

Figure 5   Nanotubes joined to larger hollow regions. (a) Intermediate magnification micrograph, (b) higher magnification image of different region, (c) sketch of the structure shown in (b).
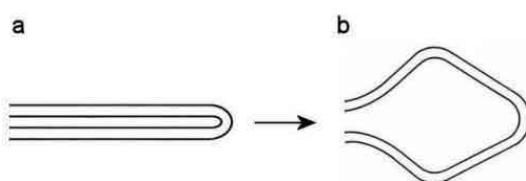

Figure 6   Schematic illustration of transformation of folded graphene sheets into hollow structure.