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Novel bilayer graphene structures produced by arc-discharge

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Abstract. A new form of carbon is described, which consists of hollow, three-dimensional shells bounded by bilayer graphene. The new carbon is produced very simply, by passing a current through graphite rods in a commercial arc-evaporation unit. Characterisation of the carbon using high resolution transmission electron microscopy is described, and the possible formation mechanism discussed.

1. Introduction

Many interesting structures, including C_{60} and carbon nanotubes, can be produced using a graphite arc-evaporation apparatus [1 - 4]. Recently, yet another kind of carbon has been discovered in graphite samples which have been subjected to arc-discharge [5 - 7]. This new carbon apparently consists of hollow graphitic shells bounded by curved and faceted planes, typically made up of two graphene layers. 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, indicating that the formation of the shells and the nanotubes is intimately connected. In this paper, this new carbon material is characterised using high resolution transmission electron microscopy, and evidence is presented that the structures are three-dimensional rather than flat. The possible mechanism whereby graphite could be transformed into the three-dimensional shells is considered, and possible applications for the new material discussed.

2. Experimental Methods

The graphene material described in this paper was prepared in a commercial arc-evaporator, the 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. 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. 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. 1 (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. 1 (b). Here, the outline of the structure is much more irregular than in the fresh graphite, with many curved and unusually-shaped features. The material is decorated with numerous short nanotubes and nanoparticles.

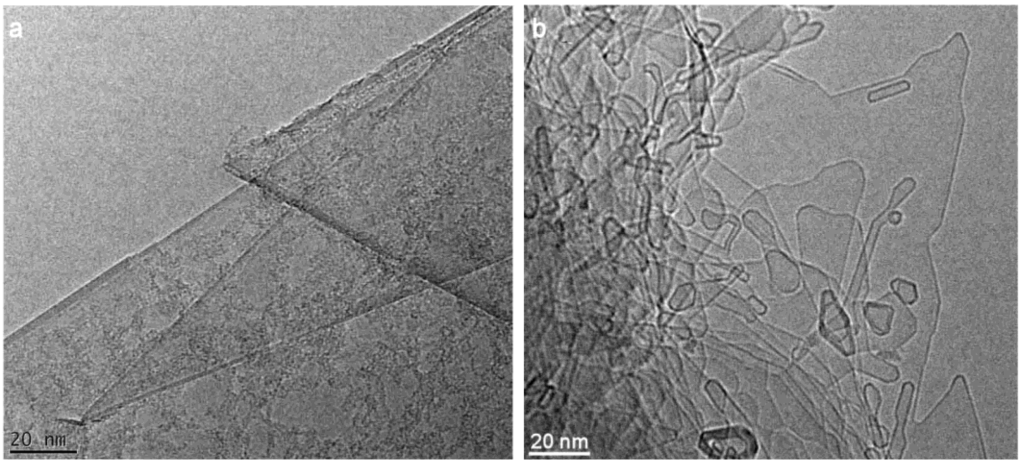

Figure 1: (a) Low magnification micrograph of carbon from fresh graphite rod. (b) Micrograph at same magnification showing transformation in structure following arc-discharge.

A higher magnification image of the material following arcing is shown in Fig. 2 (a). It can be seen that this largely consists of bilayer graphene. A striking feature of the graphitic material was that nanotubes were often observed to be seamlessly joined to the larger regions. An example can be seen in Fig. 2 (b). The tubes were generally 4 – 6 nm in diameter. This strongly suggests 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, bilayer, graphene without being seriously distorted, at least in the vicinity of the junction.

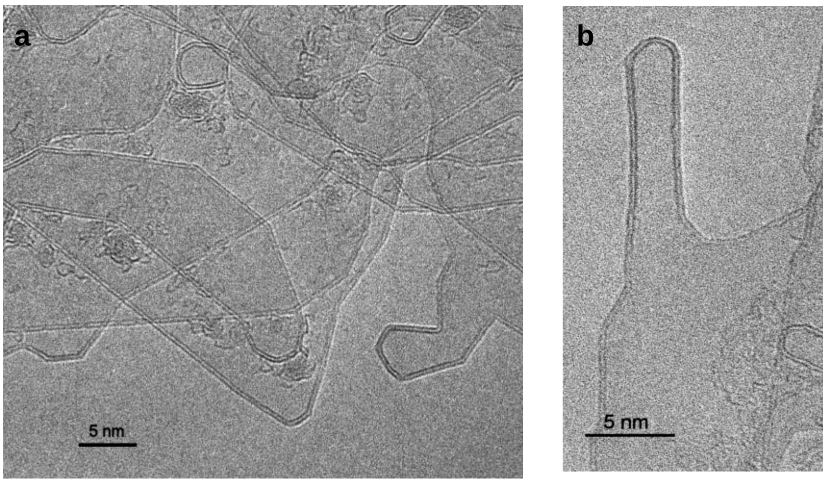

Figure 2: Higher magnification micrograph of carbon following arc-discharge. (b) Micrograph showing bilayer nanotube joined to larger region.

Another reason for believing that this novel carbon material is three-dimensional rather than flat is that nanotubes or nanoparticles can sometimes be found encapsulated inside the larger structures, showing that they are hollow. An example is shown in Fig. 3. Here, a bilayer nanoparticle can be seen apparently inside a larger bilayer structure. The way in which the contours of the nanoparticle follow those of the larger structure strongly suggests that it is encapsulated inside, rather than supported on the surface.

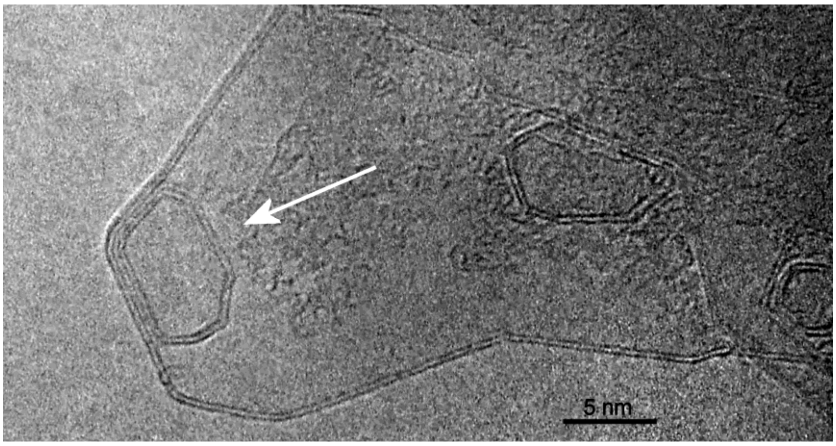

Figure 3: Bilayer graphene structure with nanoparticle apparently encapsulated inside (arrowed).

4. Discussion

The structural transformation of graphite as a result of the passage of an electric current (i.e. by Joule heating), has now been observed by a number of groups [8 - 12]. For example, Huang *et al.* [9], reported experiments in which samples of graphene prepared from highly orientated pyrolytic graphite (HOPG) were Joule-heated inside a transmission electron microscope. This produced a radical restructuring of the graphene rather similar to that described here, except that the final structures were made up of single-layer rather than bilayer graphene. Like other authors in this field, Huang *et al.* discussed the process in terms of the sublimation and edge reconstruction of flat graphene. However, as argued in this paper, there are good reasons for believing that the material produced by this transformation is in fact three-dimensional. In particular, the presence of nanotubes seamlessly joined to larger regions, and the observation of nanoparticles encapsulated inside larger graphene structures, are difficult to explain in terms of a "flat graphene" model. Obtaining clear proof that the structures are three-dimensional will require the use of electron tomography, and such experiments are planned.

If we accept that the transformation involves the growth of three-dimensional structures from initially two-dimensional graphite, what could be the mechanism? It seems likely that the key to this lies in the edge structure of graphite. It is well established that graphite planes often have "closed" edges, so that the layers resemble folded sheets [e.g. 13 - 15], as in the micrograph shown in Fig. 4 (a).

a b

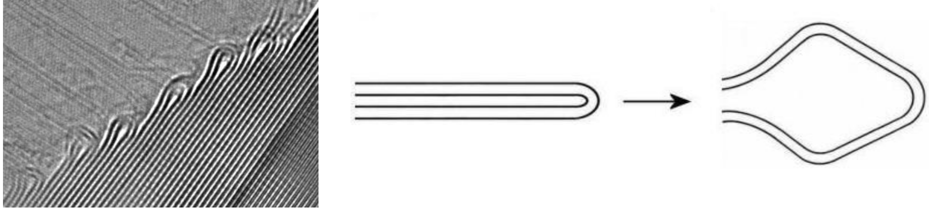

Figure 4: (a) Folded bilayer edges in graphite, reproduced with permission from ref. [15] (Suppl. data). (b) Schematic illustration of transformation of folded graphene sheets into hollow structure.

In a sense, therefore, these adjacent layers already represent closed structures, and the transformations induced by Joule-heating may simply involve an opening up of the layers to produce hollow particles, as illustrated schematically in Fig. 4(b). Such a process might be initiated at pentagonal rings which occur where zig-zag and armchair edges meet [15]. In the case of the HOPG experiments [9], we have noted that these result in the formation of structures bounded by single layers instead of the bilayers observed in the present paper. This suggests that the edge structure in HOPG differs from that in "normal" synthetic graphite, with folded monolayer rather than bilayer edges.

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References

[1] Krätschmer W, Lamb L D, Fostiropoulos K and Huffman D R 1990 *Nature* **347** 354
[2] Iijima S 1991 *Nature* **354** 56
[3] Iijima S and Ichihashi T 1993 *Nature* **363** 603
[4] Bethune D S *et al.* 1993 *Nature* **363** 605
[5] Harris P J F 2009 *J. Phys.: Condens. Matter* **21** 355009
[6] Harris P J F 2011 *Phil. Mag.* **91** 2355
[7] Harris P J F 2012 *Carbon* **50** 3195
[8] Jia X *et al.* 2009 *Science* **323** 1701
[9] Huang JY *et al.* 2009 *PNAS* **106** 10103
[10] Qi L *et al.* 2010 *Carbon* **48** 2354
[11] Barreiro A *et al.* 2012 *Nano Letters* **12** 1873
[12] Cruz-Silva E *et al.* 2013 *ACS Nano* **7** 2834
[13] Buseck P R, Bo-Jun H and Keller L P 1987 *Energy & Fuels* **1** 105
[14] Ugarte D 1992 *Chem. Phys. Lett.* **198** 596
[15] Liu Z, Suenaga K, Harris P J F and Iijima S 2009 *Phys. Rev. Lett.* **102** 015501