



Structural transformation of natural graphite by passage of an electric current



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ARTICLE INFO

Article history:

Received 3 March 2016

Received in revised form

23 May 2016

Accepted 26 May 2016

Available online 27 May 2016

ABSTRACT

Transmission electron microscopy is used to investigate the effect of passage of an electric current on the structure of a natural graphite. It is shown that the passage of a current can produce structures apparently consisting of hollow three-dimensional graphitic shells bounded by curved and faceted planes, typically made up of 2 graphene layers. A high degree of alignment is often found between these structures, in contrast to the material produced when synthetic graphite is treated in a similar way. The transformed carbon frequently contains small bilayer nanotubes, which are sometimes seamlessly joined to the larger graphene structures. In other cases the nanotubes are encapsulated inside larger graphene structures. A possible mechanism for the formation of these encapsulated tubes is proposed. Studies of the kind described here may help to understand the failure of graphene devices by Joule heating. The transformed carbon might also have a number of potential applications.

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1. Introduction

Previous studies by the present author and others have shown that the passage of an electric current through graphite or few-layer graphene can produce a dramatic structural transformation [1–9]. In this transformation, the large flat graphite crystallites are converted into more complex structures containing many novel features, often incorporating small nanotubes or nanoparticles. There is disagreement about the precise nature of this process. Some workers have interpreted the phenomenon in terms of the sublimation and edge reconstruction of essentially flat graphitic structures [1,2,7–9]. An alternative explanation is that the transformation actually involves a change from a flat to a three-dimensional structure [3–6]. Supporting evidence for the latter hypothesis has been obtained by using a combination of high-angle annular dark-field imaging and electron energy loss spectroscopy in the scanning transmission electron microscope [6].

Assuming that the carbon produced by passing an electric current through graphite is indeed three-dimensional and porous, it may have many interesting and useful properties. For example it might be useful as a catalyst support or as a hydrogen storage material. It could also be of value in electrical devices such as supercapacitors or lithium ion batteries, where its structural

stability might give it advantages over materials assembled from graphene flakes by solution or other methods. However, before such applications can be realised, a method is needed to produce the material in bulk. Previous attempts to prepare the three-dimensional carbon by passing a current through synthetic graphite [4–6] have generally resulted in yields lower than about 50%. Part of the reason for this may be that the synthetic graphite employed did not by any means consist entirely of graphite crystals: it contained a relatively high proportion of disordered carbon and particles which resembled graphitized soot. One aim of the present work is to investigate whether a higher yield can be achieved from natural graphite, which would be expected to contain much less “contamination” than the synthetic graphite.

As well as producing new carbon structures with potentially useful properties, experiments such as those described here could help us to understand the breakdown of graphite and graphene at high current densities. A number of studies have been carried out to determine the breakdown current density of graphene nanoribbons (e.g. Refs. [10–12]) but the mechanism of the breakdown is not known. A better appreciation of the mechanism would be of value in understanding the limits of graphene in electrical applications.

The starting material for the present work was natural Sri Lankan graphite. Samples were obtained from Saint Jean Carbon Inc. and from Bogala Graphite Lanka plc. A commercial carbon-coater was used to pass a current through small pieces of this graphite.

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The technique used to image the graphite before and after passage of the current was conventional high resolution transmission electron microscopy (HRTEM).

2. Experimental methods

The carbon-coater used to pass a current through the graphite samples was a Quorum Q150T ES. The electrodes in this unit are 3 mm graphite rods. In normal operation one of these rods is thinned to a diameter of approximately 1.4 mm and held in contact with the other electrode with a spring mechanism. In the present work a small piece of Sri Lankan graphite (ca. 1 mm³) was instead placed between the two 3 mm graphite rods. The chamber was then pumped by a turbomolecular pump to a pressure of approximately 3×10^{-4} mbar, and a current of 75 A was passed for 3–10 s. Samples of the Sri Lankan graphite were then prepared in two different ways for transmission electron microscopy. In order to examine the bulk structure, the whole piece of graphite was ground under isopropyl alcohol, and droplets of the suspension were pipetted onto lacey carbon films. Samples were also prepared from the surfaces of the graphite by washing the pieces of graphite with isopropyl alcohol and then pipetting a drop of the resulting suspension onto carbon films.

In order to test whether grinding the sample could produce any artefacts, samples of the treated graphite were deposited directly onto TEM grids without grinding.

The TEM used was a JEOL 2010, with a point resolution of 0.19 nm, operated at an accelerating voltage of 200 kV. At this accelerating voltage there is a danger of irradiation damage, since the threshold for knock-on damage is well below 200 kV. Experiments carried out with the samples studied here showed that visible damage occurred only after about 2 min exposure to a beam with a current density of 15 pA cm⁻². Care was taken not to expose the carbon to an electron beam for longer than this time.

3. Results

3.1. Comparison between natural and synthetic graphite

Images of the fresh Sri Lankan graphite and of the synthetic graphite used in the rods for the carbon coater were recorded. As can be seen in Fig. 1, there were significant differences between the two. The natural sample consisted almost entirely of graphite

sheets, often folded and buckled. Individual sheets were typically 3–5 μm across, containing between 10 and several 100 layers. The synthetic graphite was much less “pure” and contained large spheroidal structures, typically around 1 μm in size which resembled graphitized soot or carbon black. The graphite sheets in the synthetic material were rather smaller than in the natural graphite, generally being 1–2 μm across, with a similar number of layers. These observations confirmed that the natural graphite was a much higher quality starting material than synthetic graphite for the experiments described in this study.

3.2. Structural transformation produced by passage of current

A large number of specimens of graphite which had been treated by passage of an electric current were examined by HRTEM. In all cases the specimens contained some graphite that was apparently unaffected and some that had undergone a radical restructuring. The proportion of restructured material was much higher in samples prepared from the surfaces of the graphite than in samples prepared from the bulk. In the former, approximately 80% of the sample was wholly or partially transformed, while in the latter less than 50% was transformed. Micrographs of typical transformed areas are shown in Fig. 2. In place of the large, flat graphite sheets we have a more complex structure made up of many individual graphene crystallites. As can be seen in Fig. 2(b), these graphene structures could be 1, 2 or 3 layers thick, but in most areas the graphene was largely bilayer. A region which consists largely of bilayer graphene is shown in Fig. 3. The interplanar spacing in such bilayer structures was generally in the range 0.38–0.40 nm, somewhat larger than the spacing for graphite. The transformed carbon observed in the present study was generally less disordered than that produced from synthetic graphite. Thus, in Fig. 2(a), it can be seen that the edges of the individual graphene crystallites are mostly straight, and aligned with each other. However other regions were more disordered.

As discussed in previous papers [3–6], there are good reasons to believe that the transformed carbon is three-dimensional rather than flat, and consists of hollow shells bounded by few-layer graphene. The most direct evidence for this comes from high-angle annular dark-field (HAADF) images, including tilt sequences, recorded in a scanning transmission electron microscope [6]. Certain structural features of the transformed carbon also indicate three-dimensionality. For example, nanotubes seamlessly joined to

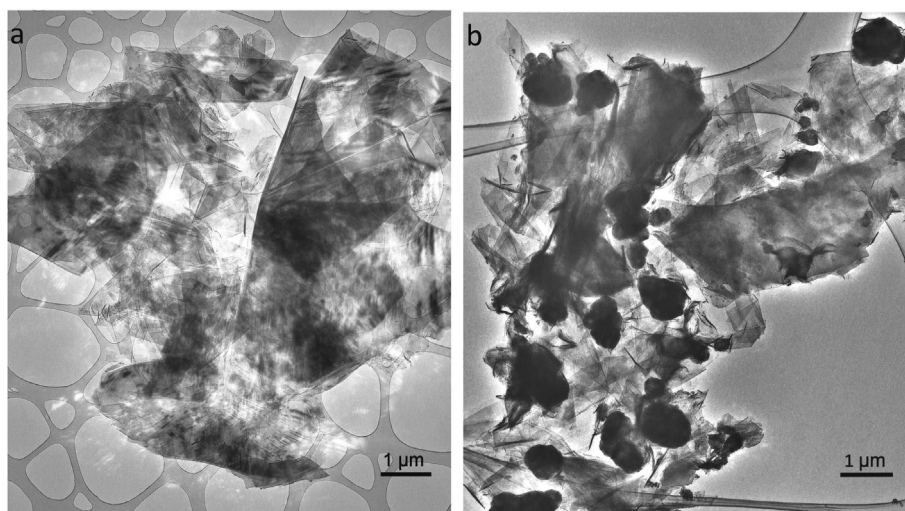


Fig. 1. (a) Low magnification transmission electron micrograph of natural Sri Lankan graphite, (b) micrograph of synthetic graphite.

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