Engineering carbon materials with electricity

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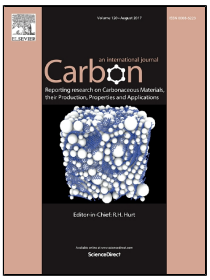

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Peter J.F. Harris

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Engineering carbon materials with electricity

Peter J.F. Harris*

Electron Microscopy Laboratory, Department of Chemistry, J.J. Thomson Building, University of Reading, Whiteknights, Reading RG6 6AF, UK.

*Corresponding author. E-mail address: p.j.f.harris@reading.ac.uk

Abstract

The passage of an electric current, or the application of an electrostatic charge, can be used to modify the structure of carbon materials in a variety of ways. The simplest example of these involves the use of high current densities to produce electrical breakdown, as a result of Joule heating or electromigration. This has been used by a number of groups to create gaps in carbon materials in order to fabricate devices such as transistors. More complex structural transformations have been observed when electric fields are applied to carbon nanomaterials. These involve the formation of carbon structures made up of single-layer or bilayer graphene with highly irregular morphologies, displaying many unusual features, including nanotube–graphene junctions. Although the nature of these transformations is disputed, they may be partly a result of electrostatic charging rather than the passage of an electric current. It has also been demonstrated that electric fields can be used to induce exfoliation of graphite, both on the nano scale and macroscopically. This article is an attempt to provide an overview of the different ways in which carbon materials can be engineered using electricity. In addition to pure carbons, work on doped and filled nanotubes is covered, and the possibility of using electric fields in "graphene origami" is discussed.

Contents

1. Introduction

Carbon and electricity have a shared history stretching back over 200 years [1]. The first electric light, the carbon arc lamp, was demonstrated by Humphry Davy some time around 1800, while incandescent electric lamps, utilising carbon filaments, were developed by Thomas Edison and Joseph Swan in the 1870s. The Hall–Héroult process, which uses carbon electrodes to smelt aluminium, was patented in 1889, and a short time later Acheson developed his electric furnace process for synthesizing graphite and silicon carbide. Today graphite is used as an anode in most batteries, and plays an essential role in power generation as a neutron moderator in nuclear reactors. Some of the most important developments in carbon science in recent decades have also involved electricity, including the bulk synthesis of C_{60} by arc discharge in 1990 [2] and the production of multiwalled carbon nanotubes in a similar way in the following year [3].

The aim of the present article is to review the ways in which carbon nanomaterials can be manipulated and modified using electricity. An attempt is made to distinguish between the

effect of passing an electric current and the effect of the application of an electrostatic charge. The passage of a current can result in Joule heating, i.e. resistive heating, and electromigration, i.e. mass transport of carbon atoms due to the momentum transfer from conducting electrons to the graphene sheets. Both phenomena can contribute to structural breakdown when a sufficiently high current density is applied, as described in Section 2. In some cases, the experiments are carried out in the presence of oxygen, which can greatly promote breakdown. Electrical breakdown has been widely applied to carbon nanotubes, to create gaps in order to create devices such as transistors. Some very skilful studies of the mechanism of electrical breakdown of nanotubes, using *in situ* TEM, have been carried out, and these are described.

Another effect which has been observed when a current is passed through a carbon nanotube is superplasticity. It has been shown that applying a stress to a single-walled carbon nanotubes (SWCNT) through which a current is being passed can result in an elongation of up to 280%. This remarkable phenomenon is discussed, together with experiments on the current-induced shrinkage of nanotubes. Outstanding work on the "plumbing" together of carbon nanotubes using an electric current is also described. The use of electrical breakdown to create gaps in graphene is then discussed, and an interesting study of the effect of passing an electric current on the structure of disordered carbons is described.

Section 3 describes effects which appear to be due, at least in part, to electrostatic charging. A number of studies over the past 8 years or so have demonstrated that dramatic structural transformations can be produced when carbon nanomaterials are exposed to an electric field at high temperatures. These transformations seem to differ from those produced by the passage of a current, and produce carbon materials made up of single-layer or bilayer graphene with highly irregular morphologies. The transformed carbons display many unusual features, including nanotube–graphene junctions and nanoparticles apparently encapsulated inside larger structures. Several studies of these transformations have now been reported, but the mechanism remains poorly understood. Some authors have suggested that the structural changes are a consequence of Joule heating, but it is argued here that electrostatic charging is the primary reason for the transformations. Theoretical work showing that the application of an electric field can reduce the van der Waals forces between adjacent graphene layers would seem to support this idea. The use of electric fields to induce the exfoliation of graphite is then discussed, and theoretical work on the ways in which fields could be used to control the

folding and unfolding of graphene structures, in what has been called “graphene origami” is summarised.

Although this review is mainly focussed on the way in which electric fields can be used to modify pure carbons, work on doped carbon nanotubes, and on material encapsulated inside carbon nanotubes is also reviewed.

2. Effects due to passage of a current

2.1 Carbon nanotubes

It is well established that both carbon nanotubes and graphene exhibit exceptionally high breakdown current densities. Values as high as 4 x 10^9 A/cm^2 have been reported for SWCNTs [4], while a figure of 10^8 A/cm^2 was found for 16 nm wide graphene nanoribbons [5]. These numbers are 2-3 orders of magnitude higher than that the values for typical metals, and are a result of the strength of the carbon-carbon bonds. When currents in excess of these values is applied, however, breakdown does occur, and can be used to modify the structures of both nanotubes and graphene in a reasonably controlled way.

Avouris and colleagues were among the first to use electrical breakdown to modify carbon nanotubes. They first applied the method to multi-walled nanotubes (MWCNTs) in 2001 [6, 7]. Breakdown was found to occur in a series of sharp current steps, as shown in Fig.1; this was attributed to the sequential destruction of individual nanotube shells. The failure was

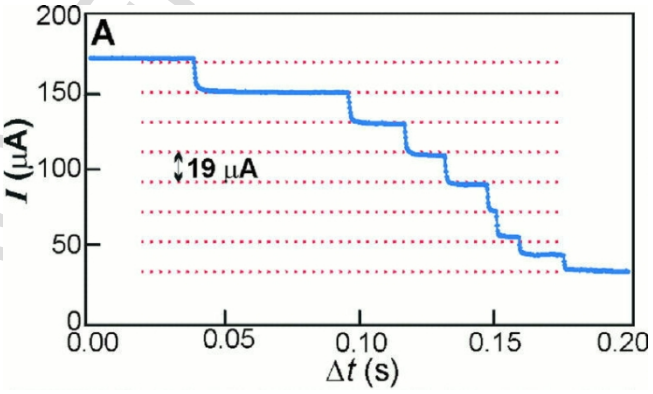

Fig. 1 Plot of current vs. time showing partial electrical breakdown of MWCNT at constant voltage, from the work of Avouris and colleagues [7].

found to occur much more readily in air than in vacuum, apparently as a result of oxidation. Thus, a 14 nm diameter MWNT experienced breakdown at a power of approximately 520 μW in vacuum and at 320 μW in air. It was noted however that breakdown in vacuum occurred much more rapidly, once initiated. The same group also used current-induced electrical breakdown to selectively remove metallic tubes from "ropes" of single-walled carbon nanotubes SWCNTs [7]. By eliminating the metallic tubes, this group were able to fabricate nanoscale circuits based solely on semiconducting SWCNTs.

Since this early work, electrical breakdown of carbon nanotubes has been quite widely studied. A number of groups have used electrical breakdown to create gaps in nanotubes. For example, Dai and colleagues fabricated transistors by depositing organic materials in electrically-created gaps in SWCNTs [8]. The size of the cut was found to be controllable by varying the lengths of the SWCNTs, and gaps as small as 2nm could be produced. In this work the cutting process was carried out under argon. Other groups have created gaps by passing a current in air [9, 10]; in such cases the breakdown is presumably due to oxidation.

The mechanism of electrical breakdown has been studied by several groups using *in situ* TEM. One of the first such studies was described by Huang *et al.* in 2005 [11]. In this work, current was passed through MWCNTs while they were being imaged inside a TEM. Breakdown behaviour was similar to that observed by Avouris *et al.* in that it occurred wall-by-wall, sometimes from the outermost wall inward, and sometimes from the innermost wall outward. In other cases, breakdown of outer and inner walls in turn was observed. Figure 2 shows an example of the breakdown of an initially 6-wall nanotube from the outermost wall inward. The current passed through the tube was initially 240 μA, and sequential drops in current were observed as the walls were removed.

Further *in situ* studies of the breakdown of MWCNTs by Joule heating were described by Jin and colleagues in 2008 [12]. A particularly interesting feature of this work was that the edges of adjacent broken shells could bond together in a so-called lip-lip interaction in order to eliminate dangling bonds. This is illustrated in Fig. 3. The first stage, shown in Fig. 3 (a) involved the formation of open edges in the outer layers, indicated by blue arrows. The upper open edge then moved downwards, as shown in (b), and formed a lip-lip connection with the other edge, indicated by the red arrows in (c). The lip-lip connections were observed to

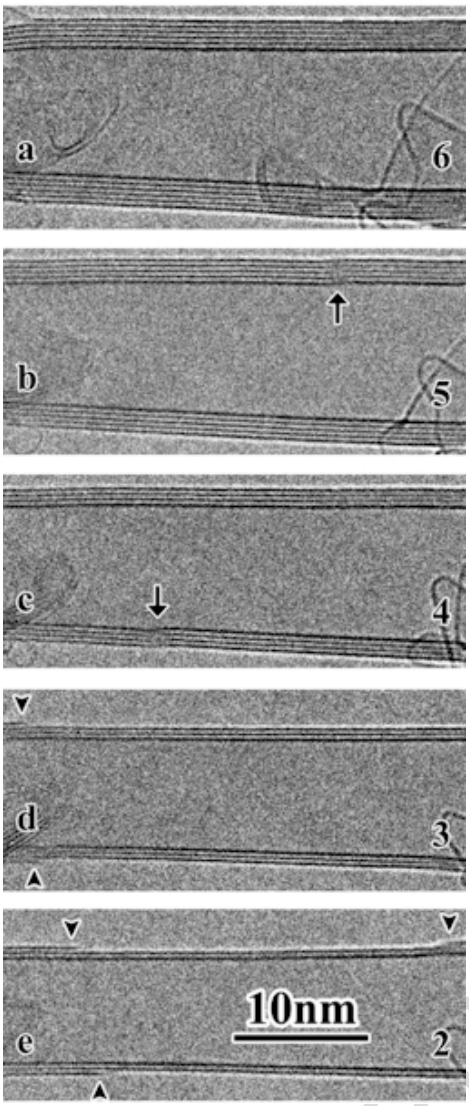

Fig. 2 (a) – (e) HRTEM images from the work of Huang *et al.* [11] showing breakdown of MWCNT as a result of passage of an electric current. Breakdown occurs sequentially from the outer to the innermost wall. The arrows mark kinks, while the arrowheads denote the residue of the 4th and the 3rd walls after breakdown.

undergo structural fluctuations, especially when a higher biased voltage was applied, as can be seen in Fig. 3 (d). These were believed to be a result of a continuous reorganization of the bridging carbon bonds at high temperature. The authors suggested that such lip-lip interactions might stabilise the open-ended growth of MWCNTs in the arc discharge process.

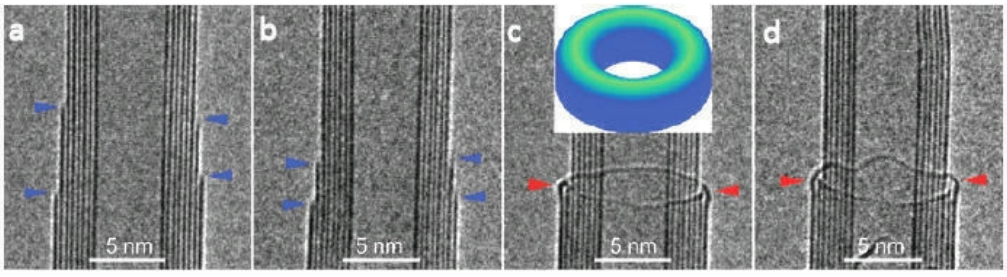

Fig. 3 (a) – (d) HRTEM images showing the formation of lip-lip bonding during breakdown of MWCNT as a result of Joule heating, from work by Jin and colleagues [12]. The inset in (c) is a schematic illustration of the lip-lip structure.

In 2006, Huang and colleagues showed that when a current is passed through a carbon nanotube it can display extraordinary plasticity [13]. These workers used a piezo manipulator to apply a stress to a SWCNT, initially 24 nm long, through which a current was being passed. At tensile failure, the SWCNT had stretched to a length of 91 nm long, representing a tensile elongation of 280%; its diameter was reduced 15-fold, from 12 to 0.8 nm, as can be seen in Fig. 4. Tensile-pulling experiments at room temperature without any electric current showed that nanotubes typically failed at a tensile strain of less than 15%. In their original paper [13], Huang *et al.* suggested that the mechanism of elongation involved the movement of 5-7 dislocation kinks through a relatively clean lattice. In subsequent work [14], Yakobson and colleagues suggested that sublimation of carbon atoms was also involved, occurring in the vicinity of 5-7 dislocation cores. Overall it seems that superplasticity in carbon nanotubes is still not fully understood, and it is not clear whether the process is promoted by the passage of a current or whether it is simply a consequence of the high temperature.

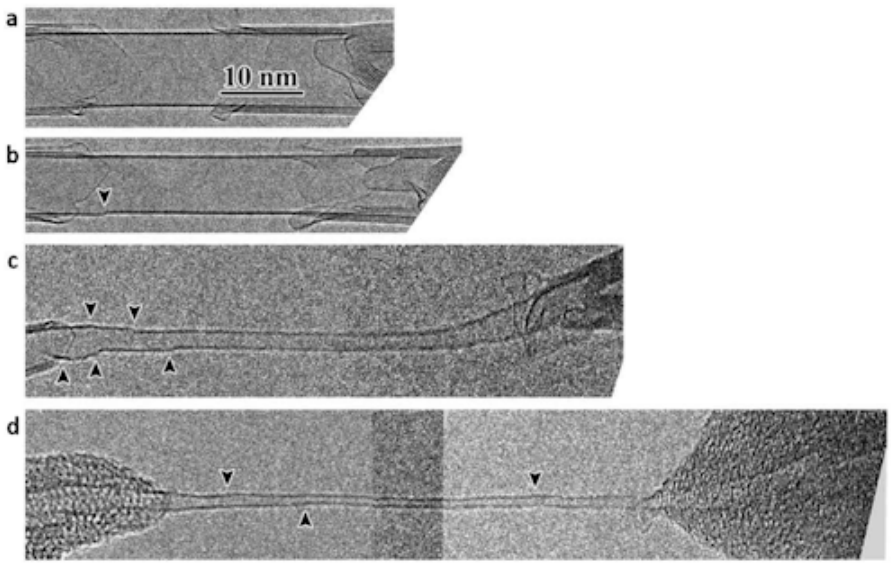

Fig. 4 (a) – (d) HRTEM images showing superplastic tensile elongation of individual single-walled carbon nanotube under a bias of 2.3 V, from the work of Huang *et al.* [13].

In a paper entitled "Shrinking a carbon nanotube", published a short time after the Huang work, Zettl and colleagues showed how a combination of Joule heating and electron irradiation could be used to dramatically reduce the diameter of carbon nanotubes [15]. Once again, this work involved the use of *in situ* TEM. Arc-grown nanotubes were positioned between electrical contacts and a voltage was applied. At voltages above of 2 V, shrinkage

was observed, and this continued until fracture occurred, as shown in Fig. 5. The precise voltages required depended on the intensity of the electron beam. The authors suggested that the shrinkage was due to a combination of knock-on damage induced by the 100 keV TEM electron beam and Joule heating and electromigration produced by the electric current. The phenomenon appears similar to that observed by Huang *et al.*, although in this case the tubes were not stressed.

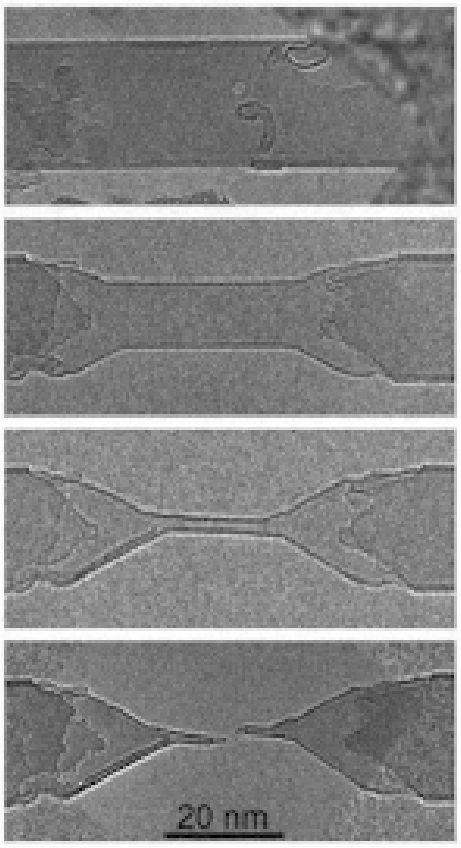

Fig. 5 *In situ* TEM images of double-walled nanotube as it shrinks and eventually fractures as a result of passage of electric current and exposure to electron beam, adapted from reference 15.

Another spectacular demonstration of how an electric current can be used to engineer carbon nanomaterials was described by Jin *et al.* in 2008 [16]. Prior to this work, the idea of joining carbon nanotubes together to create junctions which might form the basis for nanoelectronic devices had been widely discussed from a theoretical standpoint, but few examples of "plumbing" of individual tubes had been reported. Jin and colleagues showed that Joule heating could be used to connect two nanotubes, with similar diameters, in a controlled way. A piezo-driven stage was used to manipulate the nanotubes inside a TEM, and this enabled the tubes to be brought into close proximity. A current was then passed to produce the junction, as shown in Fig. 6. The authors suggested that the mechanism of the joining process involved a series of Stone–Thrower–Wales transformations and other bond rearrangements, the activation energy for which is of the order of a few eVs. They concluded that Joule

heating alone was not sufficient to produce the transformations and that electromigration must also have played a role.

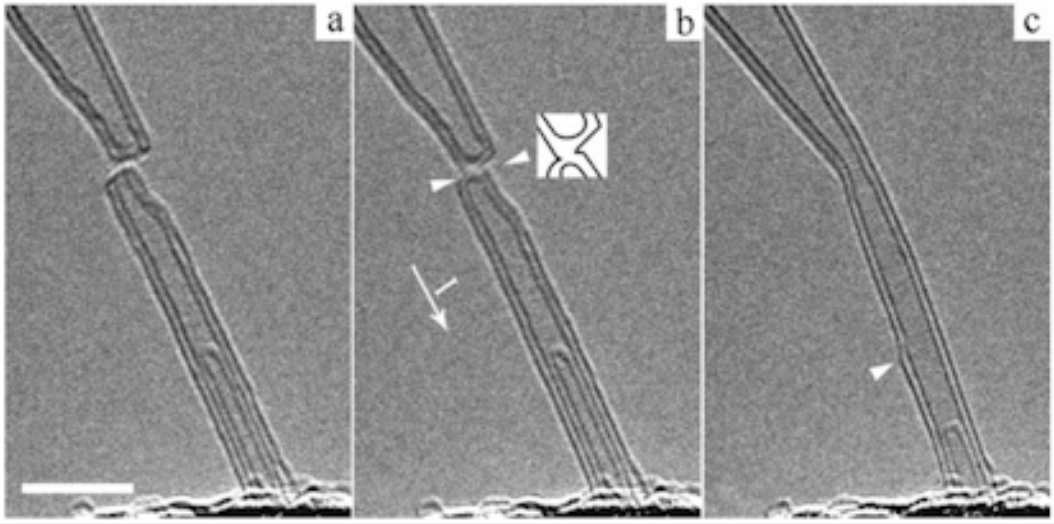

Fig. 6 Micrographs showing "plumbing" together of two DCWNTs to produce a single nanotube, from work by Jin *et al.* [16]. In (a) the two tubes can be seen being brought together. In (b) a current of ~ 20 μA, at 1.7 V, is passed and a junction begins to form as illustrated in the sketch. (c) Shows the final, continuous tube. Scale bar 5 nm.

Since the work by Jin and colleagues, a few other groups have demonstrated the joining of carbon nanotubes by the passage of a current [e.g. ref. 17] but the technique has not been widely used, owing to its experimental difficulty.

2.2 Graphene

Electrical breakdown has not yet been extensively used to engineer the structure of graphene, but several studies of the breakdown of graphene ribbons have been reported. One of the first of these was published by Murali and colleagues in 2009 [5]. These workers created graphene nanoribbons with widths down to 16 nm using electron beam lithography, and current was passed through these until breakdown occurred. Breakdown current densities of approximately 10^8 A/cm^2 were found, as mentioned above. Scanning electron microscope (SEM) images showed that breakdown occurred in the centre of the ribbons, which the authors believed pointed to Joule heating as the most likely mechanism of breakdown.

Bockrath and colleagues used pulsed electrical breakdown to create narrow gaps in suspended single- and few-layer graphene devices [18]. They then demonstrated that the junction resistance could be controlled by the application of voltage pulses, with 4 V

corresponding to an ON pulse that decreased the device resistance and 8 V corresponding to an OFF pulse that increased the resistance. Scanning electron microscopy imaging of the device showed that the gap in the ON and state was smaller than in the OFF state. It was suggested that the switching mechanism involved atomic movement and/or chemical rearrangements.

The two studies mentioned so far were carried out in a vacuum. Nanometer-sized gaps in graphene can also be produced by passing a current in air, or under a small pressure of oxygen, in which case the term "electroburning" is sometimes used. One of the first demonstrations of this was reported by Prins *et al.* in 2011 [19]. These workers created gaps 1 – 2 nm wide in few-layer graphene ribbons using a feedback controlled electroburning technique. Feedback control over the process was necessary to control the gap size: in the absence of feedback the process is self-accelerating and results in relatively large gaps. In later work, Nef and colleagues described the fabrication of sub-5 nm gaps in single-layer graphene by carrying out electroburning under a small oxygen pressure under a vacuum of $\approx 10^{-5}$ mbar [20]. They found that using these conditions gave them more control than carrying out the process in ambient air. An interesting study of electroburning of graphene was described by Sadeghi *et al.* [21]. They found that the conductance of electroburnt junctions showed a surprising increase just before breaking. They attributed this to the formation of a picoscale current path formed from a single sp^2 bond.

There is growing interest in the use of electroburning to engineer graphene structures, although achieving the delicate degree of control required is clearly a challenge.

2.3 Disordered carbon

Relatively little work has been carried out on the effect of passing an electric current on the structure of disordered carbons. One of the few such studies was described by Huang *et al.* in 2006 [22]. In this work, a current was passed through disordered carbon nanowires inside a TEM, resulting in the formation of graphitized structures, some of which were tubular in form (see Fig. 7). However, it is not clear whether the electric field was responsible for the formation of tubular structures, or whether this was simply a consequence of the extended shapes of the original amorphous carbon precursors. Marks *et al.* carried out a theoretical analysis of the evolution of amorphous precursors into carbon nanostructures and showed that for a one-dimensional amorphous precursor the final structure was tubular [23]. This was

confirmed in subsequent work by the same group [24]. Since there is little evidence that amorphous "nanorods" are preferentially formed in the arc, Huang's work may not provide a realistic model of the formation of nanotubes by arc-discharge. However, the synthesis of nanotubes from amorphous carbon deposited onto InAs nanowires has been demonstrated [25].

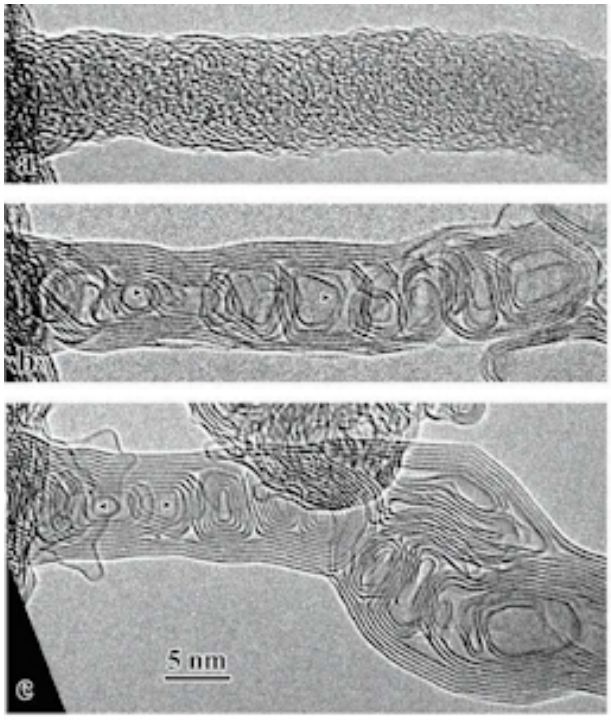

Fig. 7 Micrographs illustrating effect of Joule heating on structure of amorphous carbon, from work by Huang *et al.* [22]. (a) Amorphous carbon nanowire produced by electron-beam deposition, (b) structure after Joule heating at power of 180 μW, (c) after further Joule heating at 320 μW.

3. Effects apparently due to electrostatic charging

3.1 Structural transformation induced by electric field

Three studies published in 2009 described dramatic structural transformations induced by the application of an electric field to graphite [26 - 28]. These transformations appeared to be of a different kind to those previously observed. Two of these studies involved the *in situ* heating of few-layer graphite ‘‘nanoribbons’’ inside a TEM. In both cases it was found that the graphite ribbons evolved into complex structures which largely seemed to be made up of single-layer graphene. Examples of the transformed structures, taken from both papers, are shown in Fig. 8. The third study, by the present author, involved a TEM

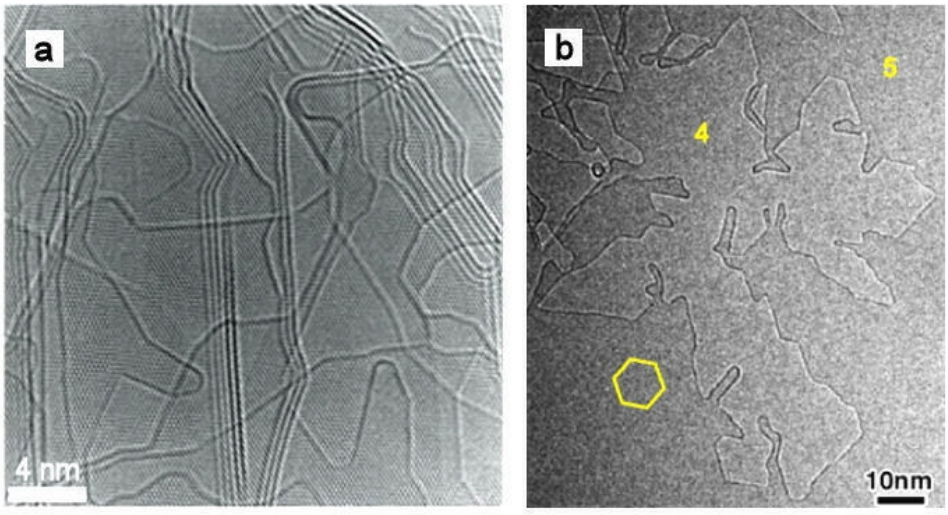

Fig. 8 (a) Structure produced by *in situ* Joule heating of graphitic nanoribbon inside a TEM, from the work of Jia *et al.* [26]. (b) Structure produced in a similar way by Huang *et al.* [27]. The numbers 4 and 5 in this figure indicate regions which the authors believe to contain 4 and 5 bilayers, respectively. The hexagon marks the orientation of the 6 equivalent {1100} planes.

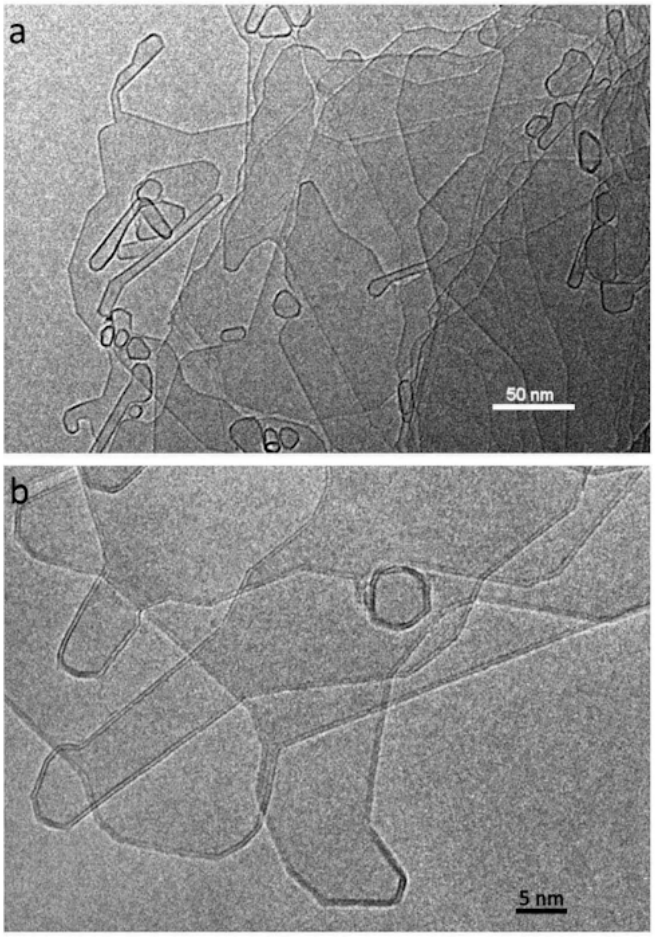

Fig. 9 Micrographs showing carbon material produced by exposing graphite to an electric field at high temperature. (a) Moderate magnification image, (b) high magnification image showing bilayer structure.

investigation of bulk graphite following exposure to an electric field. In this case the transformed carbon mainly consisted of bilayer graphene structures. Examples of the kind of structures observed are shown in Fig. 9. Following this initial work, several further studies of the phenomenon have been published [29 - 36]. There is disagreement about the nature of the transformation. One view is that the phenomenon involves sublimation and edge reconstruction of essentially flat graphitic structures [26, 27, 33 - 36]. Thus, Huang and colleagues [27, 33, 34] proposed that the morphologies observed in the transformed material could be understood in terms of a fractal-like structure produced by sublimation and reconstruction, while Jia *et al.* [26, 36] highlighted the importance of zig-zag or armchair edges in stabilizing the transformed structures. A quite different hypothesis has been put forward by the present author and colleagues [29 - 32], namely that the transformation actually involves a change from a flat to a three-dimensional structure.

There are a number of reasons for believing that the transformed 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, as shown in Fig. 10 (a) and that nanotubes are often found to be seamlessly joined to the thin shells, as in Fig. 10 (b). Direct evidence for the idea that the structures are three-dimensional 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 [31]. A discussion of the possible mechanism of the transformation of flat graphite into a three-dimensional structure is given in the next section.

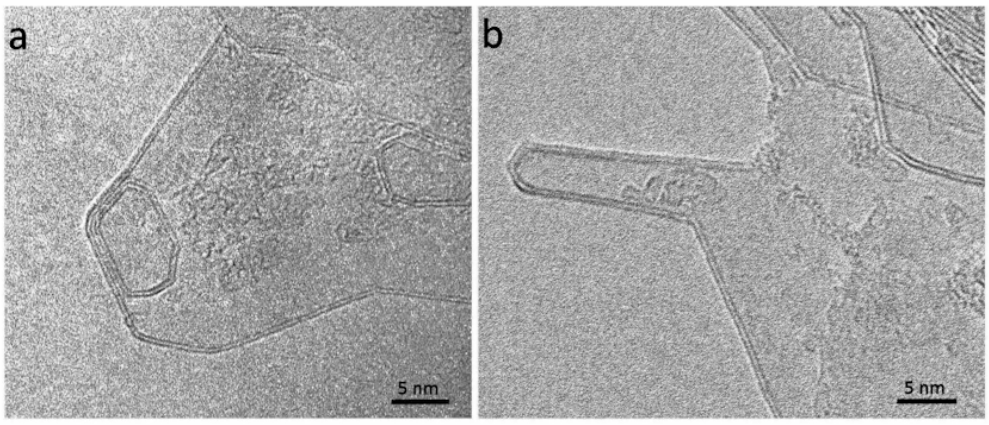

Fig. 10 Structures in graphite transformed by exposure to an electric field. (a) Bilayer graphene structure, apparently hollow with bilayer nanoparticle inside, (b) bilayer nanotube joined to larger graphene structure [32].

Recently, an interesting study of the effect of an electric field on the structure of carbon nanofibers has been published by Wang *et al.* [37]. The nanofibres were synthesized using chemical vapor growth, a process that tends to produce fibres with a relatively low degree of graphitization. Their work was primarily concerned with improving the graphitization of the fibres by the passage of a current, and it was shown that the conductivity could be increased

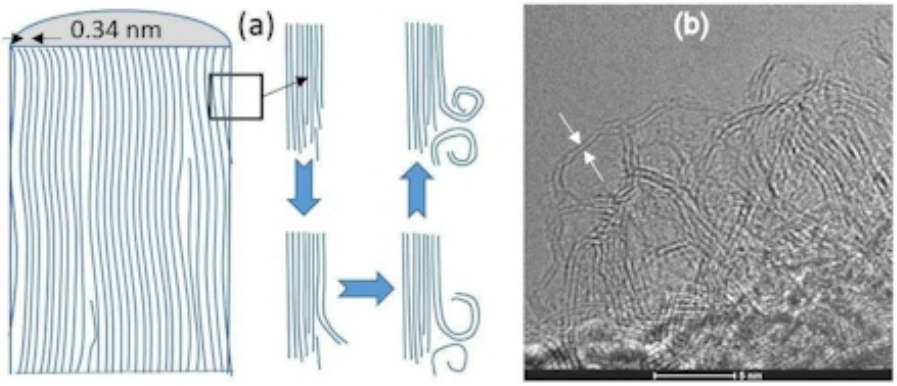

Fig. 11 (a) Schematic illustration of electrostatic exfoliation mechanism for surface layers of carbon nanofibres, (b) micrograph showing structure of exfoliated carbon. From work by Wang *et al.* [37].

by 3 orders of magnitude by employing current densities up to 10^6 A/cm^2. Higher current densities led to the exfoliation of mostly bilayer graphene flakes from the skin of the graphitic nanofibers, as shown in Fig. 11. The formation of bilayer graphene structures is reminiscent of the work on the transformation of bulk graphite described above. Wang and colleagues suggested a mechanism in which individual layers in the fibres accumulated electrostatic charge, and this charge accumulation led to the exfoliation of the surface layers. This would seem to be a highly plausible explanation for the phenomenon observed by Wang *et al.*, as well as for the other structural transformations described in this section.

3.2 The mechanism of structural transformation

This section considers in more detail the mechanism of the electric field-induced transformations described above. It is assumed that the process involves an evolution from a flat to a three-dimensional structure rather than sublimation and edge reconstruction of flat graphene. In discussing mechanism it is helpful to consider the edge structure of graphite. It is well established that graphite planes often have ‘‘closed’’ edges, so that the layers resemble folded sheets [38 - 42], as illustrated in Fig. 12 (a). The transformations reported in the previous section may simply begin with an ‘‘opening’’ of the layers, as shown

schematically in Fig. 12 (b). Supporting evidence for this mechanism, is provided by images showing the early stages of the process, as shown in Fig. 12 (c). The question arises, therefore, of why the application of an electric field should result in the opening of the graphite layers. It was pointed out by the present author that the phenomenon is reminiscent of the separation of gold leaves in an electroscope [32], although it was not clear whether this

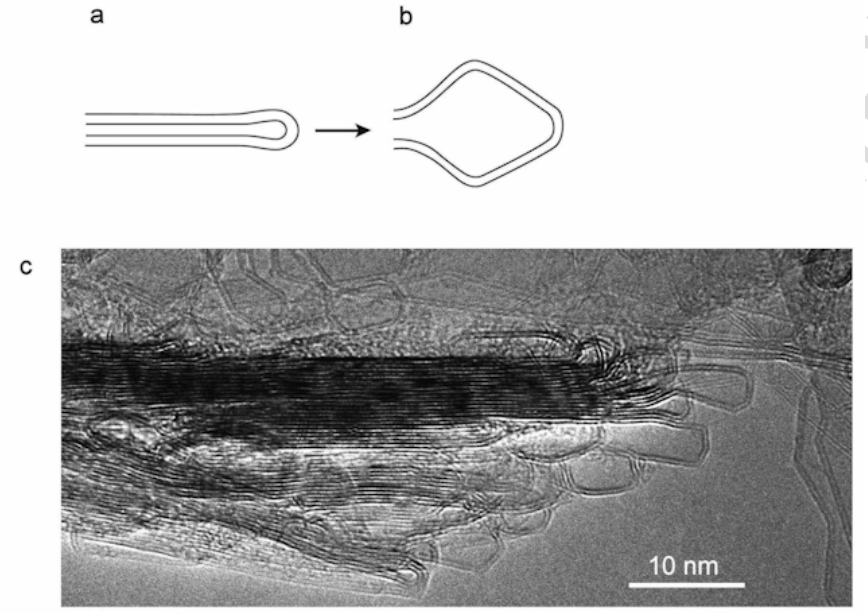

Fig. 12 (a) and (b) Schematic illustration showing suggested mechanism for transformation of folded graphene sheets into hollow structure, (c) HRTEM image of graphitic region edge-on, apparently showing early stages of transformation [31].

was relevant. As noted above, Wang *et al.* have suggested that an analogous process is indeed involved, in which charge accumulates in the graphene layers, leading to repulsion between the layers and separation. This idea is supported by theoretical work which shows that an external field applied perpendicular to a pair of graphene layers can drive the system to a unstable state where the layers are decoupled and can be easily separated [43, 44].

One of the most interesting features of graphite transformed by an electric field is the presence of nanotubes joined to graphene shells, as shown in Fig. 10 (b). A detailed analysis of these junctions has been carried out and has shown that the junction angles are not random but fall close to multiples of 30° [45]. It was demonstrated that connections with these angles are the only ones which are consistent with the symmetry of the hexagonal lattice, and molecular models showed that a continuous lattice requires the presence of large carbon rings at the junction. The possible formation mechanism of the junctions was also discussed, and it

was suggested that the process might be initiated at the pentagonal rings which are believed to occur where a zigzag edge meets an armchair edge.

3.3 Electrostatic exfoliation

The exfoliation of graphite to produce graphene has been the subject of a huge amount of work [46], but there have been relatively few studies on the use of electric fields to induce exfoliation. Liang and co-workers were among the first to explore this approach. In 2009 they described the use of electrostatic exfoliation to deposit patterned few-layer graphene onto a substrate [47]. Their method involved firstly creating patterns on the surface of a highly oriented pyrolytic graphite (HOPG) disc using lithographic techniques. A feature of the pattern was then brought into contact with an SiO_2/Si substrate and a voltage was applied between the HOPG template and the substrate. This resulted in exfoliation of graphene flakes from the HOPG, and attachment to the substrate. Using this technique the authors demonstrated the exfoliation/printing of 18 nm wide graphene "nanolines", which could be used to fabricate nano transistors.

Two recent studies have explored different methods of electric field-induced exfoliation. Rubio-Verdú and colleagues showed that a scanning tunneling microscopy (STM) tip could be used to locally exfoliate HOPG by applying an electrostatic force at the edge of a terrace, forming triangular flakes [48]. Macroscopic exfoliation of graphite was demonstrated by Gao *et al.* [49]. In this work a voltage of around 20 kV was applied to graphite rods held under water. This resulted in an explosion which produced a variety of carbon species including few-layer and monolayer graphene sheets. These interesting studies suggest that the technique of electrostatic exfoliation deserves further research.

3.4 Graphene origami

The concept of graphene origami was first put forward in a 1995 paper by Ebbesen and Hiura [50]. In this paper, which anticipated the "discovery" of graphene by 9 years, scanning probe microscopy was used to create folds in graphene layers on the surface of highly ordered pyrolytic graphite. While this represented a significant technical feat, the resulting structures were still essentially two-dimensional. In 2014 Zhu and Li showed how, in theory, an electric field could be used to create three-dimensional graphene "nanocages" [51]. Their simulation began with a double cross-shaped graphene flake, as shown in Fig. 13 (a). Hydrogen atoms were then added around the edges of the flake, and at the junctions between the square

sections. They then showed that the structure could be reversibly closed and opened by the application of an external electric field, due to the polarization of carbon atoms. The closed nanocage is shown in Fig. 13 (b). It was suggested that the cages could be used for high-density hydrogen storage.

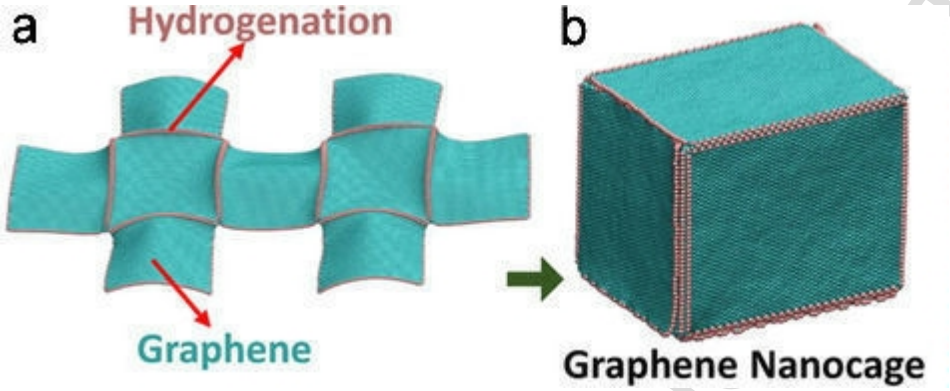

Fig. 13 Illustration of folding of hydrogenated graphene structure to form closed nanocages, induced by electric field, from the work of Zhu and Li [51].

4. Experiments with doped and filled nanotubes

In a study published in 2006 [52], Peng *et al.* prepared amorphous carbon nanowires using a similar method to that of Huang *et al.* [22], and deposited Fe particles onto the wires. A current was then passed through these structures and this caused the Fe particles to move along the nanowires, resulting in graphitization. The breakdown current density of the original amorphous nanowires was found to be 2.2 x 10^5 A/cm^2, but this increased to 4.6 x 10^8 A/cm^2 for the graphitized nanowires. This figure is comparable to the values found for nanotubes and graphene ribbons (see above), suggesting that the graphitized nanowires could be useful in nanoelectronic applications.

Grobert and colleagues have explored the effect of Joule heating on nitrogen and boron-doped carbon nanotubes and on filled nanotubes [53 - 55]. In the first of these studies [53], N-doped carbon nanotubes, grown catalytically, were subjected to Joule heating inside a TEM. The initial N-MWCNTs were rather disordered and often had a bamboo-like structure. Figure 14 shows the effect of passing a current of 47 μ A at 2000 mV through an individual tube. It can be seen that the structure becomes progressively more ordered. There is also evidence for the formation of single-layer material which resembles some of the "three-

dimensional graphene" structures discussed in Section 3.1 above. At sufficiently high current densities the nanotubes fractured, often leaving conical tips. The structure of these tips appeared to be related to the nature of the "compartments" in the original tubes.

As well as imaging the N-MWCNTs, Grobert *et al.* used electron energy loss spectroscopy (EELS) to determine the nitrogen content of the tubes before and after Joule heating. The as-produced tubes were found to contain approximately 3% N, but the N was completely removed by the passage of current. The restructuring and loss of N resulted in a significant increase in the conductivity of the tubes.

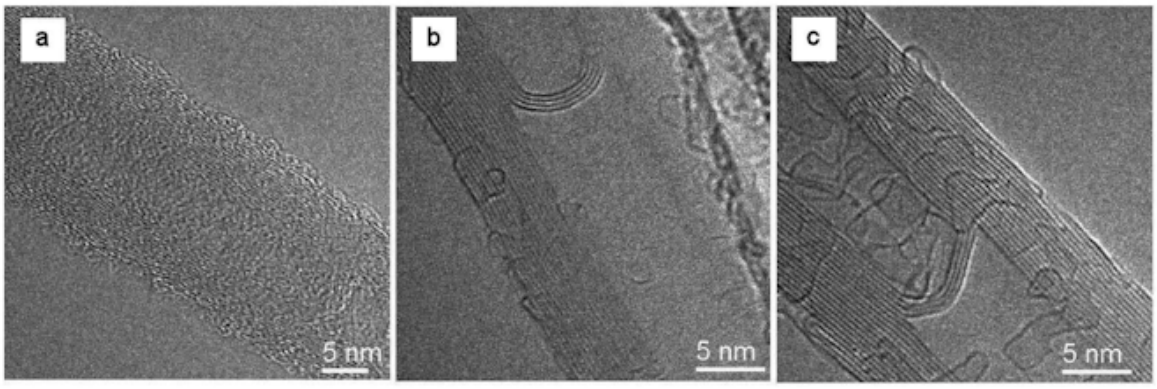

Fig. 14 Images showing nitrogen-doped MWCNT before (a) and during (b), (c), the application of current, from work by Grobert and colleagues [53].

The same group carried out a similar study of boron-doped MWCNTs [54]. Again the passage of current resulted in restructuring of the tubes, and in loss of the dopant, although some B was retained in the tubes after Joule heating. As in the case of the N-doped tubes, the passage of current resulted in changes in the electrical behaviour of the B-MWCNTs, and high current densities resulted in fracture of the tubes. Both of these studies show that care needs to be taken to limit the maximum current density if doped-MWCNTs are to be used in electronic applications.

Some interesting work has been carried out on the passage of a current on filled carbon nanotubes. Costa and colleagues used a nanomanipulator inside a TEM to make connections between electrodes and filled tubes, and then showed that passing a current could induce the transport of the filling along the tube [56], an effect similar to that previously reported by

Peng *et al.* [52]. In subsequent work [57] the same group showed how experiments with filled tubes could be used to determine the temperatures which were generated by the passage of current. Multiwalled nanotubes filled with a low vapour pressure material, namely $Zn_{0.92}Ga_{0.08}S$, were used in this work. Two different configurations were used: one with the tube connected at both ends, and one with an electrode connected to a side wall. In both cases the passage of a current resulted in the expulsion of the filling material. Figure 15 shows the effect of Joule heating on a nanotube connected at both ends. Initially, sulphide is removed from the area close to the Au cathode. Then a "hotspot" develops further along the tube, creating a gap in the filling as sulphide vaporises (Fig. 15 (b)). The two segments are then progressively consumed by the expansion of the hotspot (Fig. 15 (c)). The segment fronts acted as markers for the sulphide sublimation temperature (928 K). Further

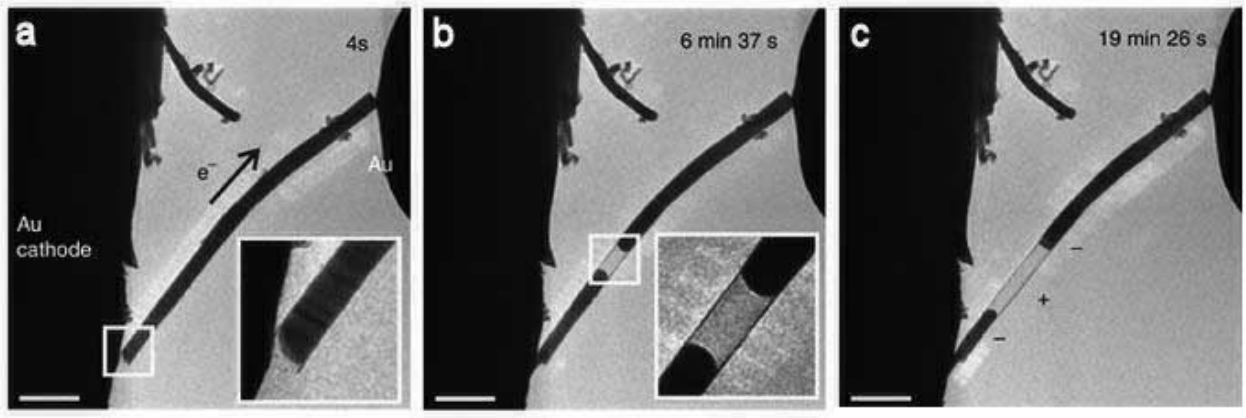

Fig. 15 Micrographs illustrating electrically induced removal of $Zn_{0.92}Ga_{0.08}S$ from inside of MWCNT. Plus and minus signs in (c) refer to temperatures above and below the sublimation point of the core. Scale bar 0.5 μm. From work by Costa *et al.* [57].

detailed studies of filled tubes enabled Costa *et al.* to determine, for the first time, the radial heat distribution inside CNTs.

In more recent work, the Grobert group has shown how the structure of Cr_2O_3 encapsulated inside MWCNTs can be transformed by Joule heating of the filled tubes [55].

5. Discussion

A very large amount of work has been carried out on the modification of carbon nanomaterials using electricity and this article is not intended to be an exhaustive review. Instead, an attempt has been made to highlight some of the most significant and striking

results in this field, and to distinguish between the effect of passing an electric current and the effect of the application of an electrostatic charge. The passage of current has been used to create gaps in nanotubes and graphene by inducing breakdown. The opposite process, i.e. the plumbing together of nanotubes by passing a current through them, has also been demonstrated. While many of these laboratory demonstrations are extremely impressive, there is still a long way to go before similar techniques can be used to create useful electronic devices containing thousands or millions of connections.

The discovery of "superplastic carbon nanotubes" by Huang *et al.* [13] created wide interest. The demonstration that carbon nanotubes can be stretched by almost 280% when a current is passed through them at high temperatures came as a surprise, given that the room temperature breaking strains of carbon nanotubes are typically around 10%. It is not clear whether the remarkable ductility observed in these experiments was a result of the high temperature, the electric current, or both. More work on this phenomenon would be welcome.

There has been growing interest recently in the massive restructuring of carbon materials which can be induced by the application of an electric field to graphite or to few-layer graphene. This phenomenon was discovered independently by three groups in 2009 [26 - 28], and involves the formation of a carbon material with a highly irregular edge morphology, with many re-entrant structures and unusual features including nanotubes seamlessly joined to larger graphene regions. The precise mechanism of this restructuring is still a matter of debate. It has been argued here, and in previous papers, that the process involves an evolution from a flat to a three-dimensional structure rather than sublimation and edge reconstruction of flat graphene, as has been suggested by other authors. It has also been argued that this transformation is initiated when charge accumulates in the graphene layers, leading to repulsion between the layers and separation, a suggestion that was first made explicitly by Wang *et al.* [37]. However, this is far from full explanation of the phenomenon. One of the most remarkable aspects of the transformation is the extreme fluidity of the carbon structures when exposed to an electric field at high temperatures. This can be seen graphically in the videos which accompany reference 27. In some ways this resembles the superplasticity observed by Huang and colleagues; neither phenomenon is well understood.

It is clear that the application of an electric field can promote dramatic restructuring of carbon materials, but the transformations produced in this way are uncontrolled, creating essentially

random structures. This contrasts with the very precise control, on the nm scale, which can be achieved by electrical breakdown. Is it possible to envisage a way in which the more controlled application of a field could be used to engineer defined, three-dimensional carbon structures? The intriguing theoretical work by Zhu and Li on "graphene origami" shows one way in which an electric field could be used to create 3D graphene structures with defined shapes [51]. While carrying out graphene origami experimentally may be beyond our present capabilities, theoretical work of this kind shows that the application of electric fields could have great potential for the controlled manipulation of graphene on the nanoscale.

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