

Structural transformation of natural graphite by passage of an electric current

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Structural transformation of natural graphite by passage of an electric current

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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 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. [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. 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 75A 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 200kV. At this accelerating voltage there is a danger of irradiation damage, since the threshold for knock-on damage is well below 200kV. Experiments carried out with the samples studied here showed that visible damage occurred only after about 2 mins 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 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 the larger graphene structures are often seen. An example is shown in Fig. 4. 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. A detailed analysis of these junctions is currently being carried out [13].

As well as nanotubes joined to graphene structures, many discrete nanoparticles or nanotubes were present in the transformed carbon. The nanotubes were often found to be aligned with the edges of the larger graphene structures, as can be seen in Fig. 5. Clusters of tubes aligned with the graphene edges were also seen, as shown in Fig. 6. Some of these nanotubes were undoubtedly supported on the surfaces of the graphene and in such cases the alignment may

be due to lattice matching between tubes and graphene, as discussed by Ortolani *et al.* [14]. In other cases it seems that the nanotubes were encapsulated inside hollow graphene structures. The tube shown in Fig. 5(b) may be an example. This tube is exactly aligned with the edge of a bilayer graphene structure, and separated from the graphene by a distance close to the graphite interplanar spacing, strongly suggesting that it is inside the structure rather than on top. Examples of nanotubes and nanoparticles apparently encapsulated inside hollow graphene structures have been shown in previous papers (e.g. Fig. 4 of reference [5]). The possible formation mechanism for such tubes is discussed in the next section.

3.3 The effect of grinding

Examination of treated graphite prepared without grinding showed that it had exactly the same structure as the material prepared by grinding.

4. Discussion

It has been demonstrated that the passage of an electric current through a small piece of natural graphite, approximately 1 mm³ in size, can produce a striking structural transformation. This transformation is more noticeable in samples collected from the surface of the piece of graphite than from the bulk, for reasons which are not fully understood. In the surface samples, the proportion of transformed carbon was roughly 80%.

The transformation of the natural graphite is similar in many ways to that observed with synthetic graphite [4 – 6]. There are good reasons to believe that the process involves the formation of three-dimensional, hollow, structures bounded by few-layer graphene walls, as discussed above. Since the graphene in the transformed carbon is mainly bilayer, we can refer to the material as “three-dimensional bilayer graphene” (3DBG). A possible mechanism for the restructuring has been put forward which involves an “opening” of the layers of graphite, beginning at the edges. It is well established that graphite layers often have “closed” edges, so that the layers resemble folded sheets [15-19], as illustrated schematically in Fig. 7(a). An image of the fresh Sri Lankan graphite in which some closed edges can be seen is shown in Fig. 8. Some workers have suggested that a single graphene sheet can curl back on itself to form a tube [20], and evidence for such scroll-like structures has been presented in a study of free-standing graphene imaged with the electron beam perpendicular to the graphene planes [21]. However, the image in Fig. 8, in which the beam is parallel to the graphite planes appears to show adjacent sheets closed at the edges, rather than scrolls. Fig.

7(b) illustrates the beginning of the opening process. In previous work, micrographs apparently displaying the early stages of transformation have been shown (e.g. Fig. 8 of reference [6]).

A notable feature of the material produced from natural graphite is a greater degree of alignment of the graphene structures with each other, as can be seen in Fig. 2. This perhaps reflects the higher crystallinity and larger crystallite sizes in the natural compared to the synthetic graphite. Another interesting feature is the presence of short nanotubes, often bilayer, either supported on or encapsulated inside larger graphene structures. These tubes were often found to be aligned with the edges of the larger graphene structures, and this suggests a possible formation mechanism similar to that illustrated in Fig. 9. Here, the starting material is a 6-layer graphite sheet with closed edges. The first stage in this process, shown in (a) and (b), is the opening of the layers near the edge followed by a knitting together of the 2 inner layers to form a tube, as shown in (c). As can be seen in Figs. 5 and 6, most of the tubes are quite short, so a “capping” process must also occur, resulting in the formation of multiple tubes parallel to the graphene edge. Many details of this process, and of the transformation in general, remain poorly understood, not least why the passage of an electric current should result in the opening of the graphite layers. The phenomenon is reminiscent of the separation of gold leaves in an electroscope, although whether this has any relevance to the present case seems doubtful.

It is interesting to consider possible applications for three-dimensional graphenes such as that described here. As we have seen, these new carbons apparently consist of hollow graphitic shells bounded by curved and faceted planes, chiefly made up of 1 - 3 graphene layers. This structure gives the material a very high surface area, and large internal volume, suggesting it may have potential as a catalyst support or as a hydrogen storage material. Concerning the latter application, it is worth noting that carbon nanohorns, which are structurally quite similar to the carbon discussed here, are considered to be very promising materials for hydrogen storage [22, 23].

Another area for which the material appears particularly suitable is as an electrode material for supercapacitors. Compared with microporous carbon, which has traditionally been used in supercapacitors, three-dimensional bilayer graphene has relatively large pore sizes (typically of the order of a few 10s of nm), which would greatly facilitate the penetration of electrolyte

ions into the pores. The structure of 3DBG also suggests it will have a much higher electrical conductivity than microporous carbon. Three-dimensional bilayer graphene also has advantages over three-dimensional graphene materials produced by assembling small fragments of graphene using aqueous methods (e.g. [24, 25]). In these materials the 3D structure is reliant on weak forces such as van der Waals interactions, and they therefore lack mechanical strength. The graphene walls also have a tendency to “clump together”, destroying the porosity. Three-dimensional bilayer graphene on the other hand is largely a continuous material in which the porosity is a result of pentagonal and other non-hexagonal carbon rings in the graphene structure, and would be expected to have far higher stability and superior mechanical properties.

Before any of these applications can be realised it will be necessary to develop methods for bulk synthesis of the transformed carbon. The results presented here represent some progress towards that aim. It has been shown that around 80% of the surface regions of the graphite samples can be transformed by the passage of current. It is possible that similar levels of transformation of the bulk could be achieved by using higher currents, or by passing the current for longer times. If so, then scale-up to bulk production may be achievable.

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Figure captions

- Figure 1** (a) Low magnification transmission electron micrograph of natural Sri Lankan graphite, (b) micrograph of synthetic graphite.
- Figure 2** (a) Intermediate magnification micrograph of natural graphite following passage of current, (b) high magnification micrograph of same sample.
- Figure 3** Micrograph of transformed carbon showing region consisting largely of bilayer structures.
- Figure 4** Nanotube seamlessly joined to larger hollow region.
- Figure 5** (a), (b) Micrographs showing few-layer nanotubes aligned with graphene edges.

- Figure 6** Micrograph showing clusters of nanotubes aligned with graphene edges.
- Figure 7** Schematic illustration of transformation of folded graphene sheets into hollow structure.
- Figure 8** Micrograph of fresh Sri Lankan graphite showing evidence of closed edges.
- Figure 9** Schematic illustration of formation of bilayer nanotube at graphite edge.

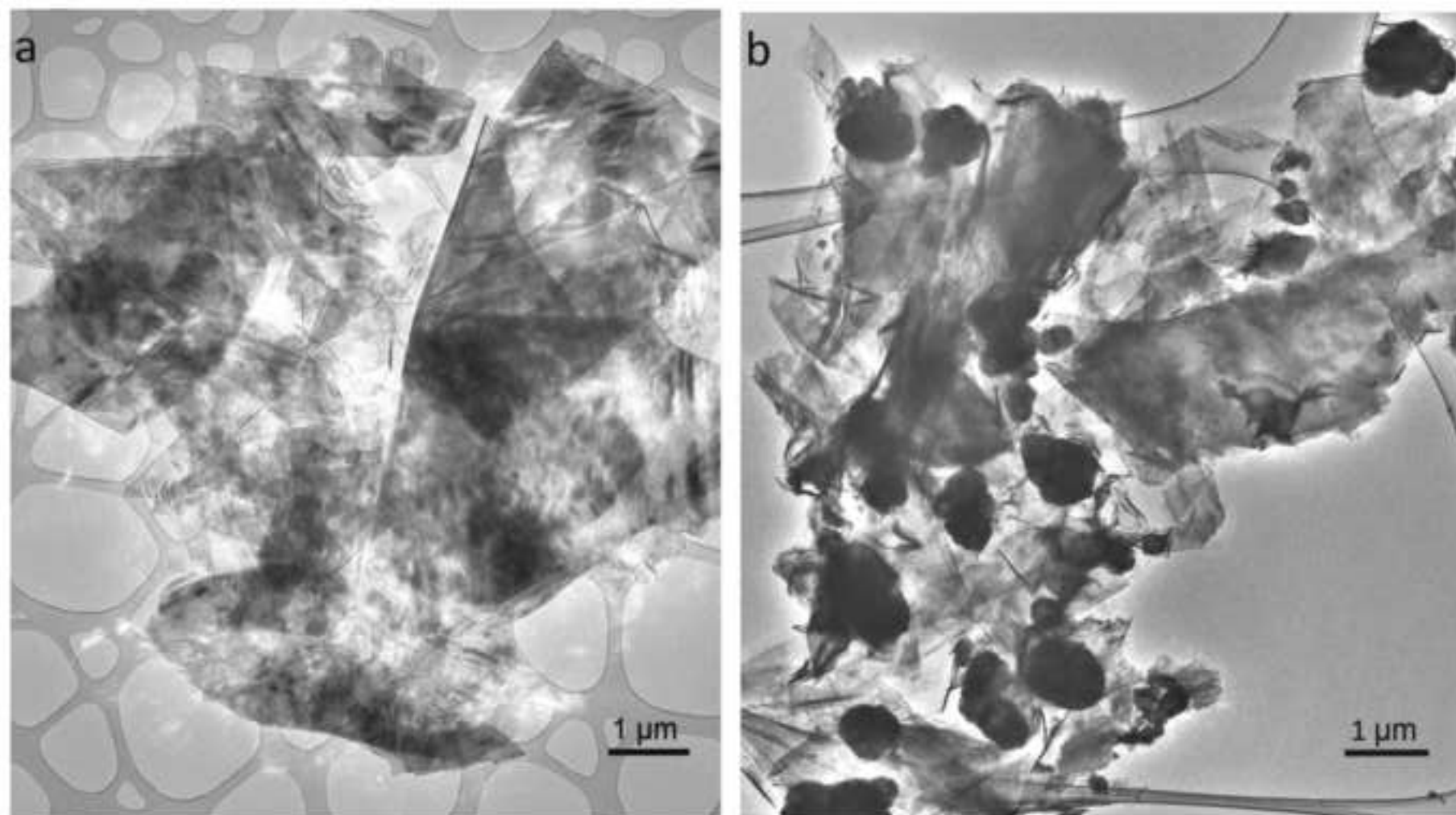


Fig. 1

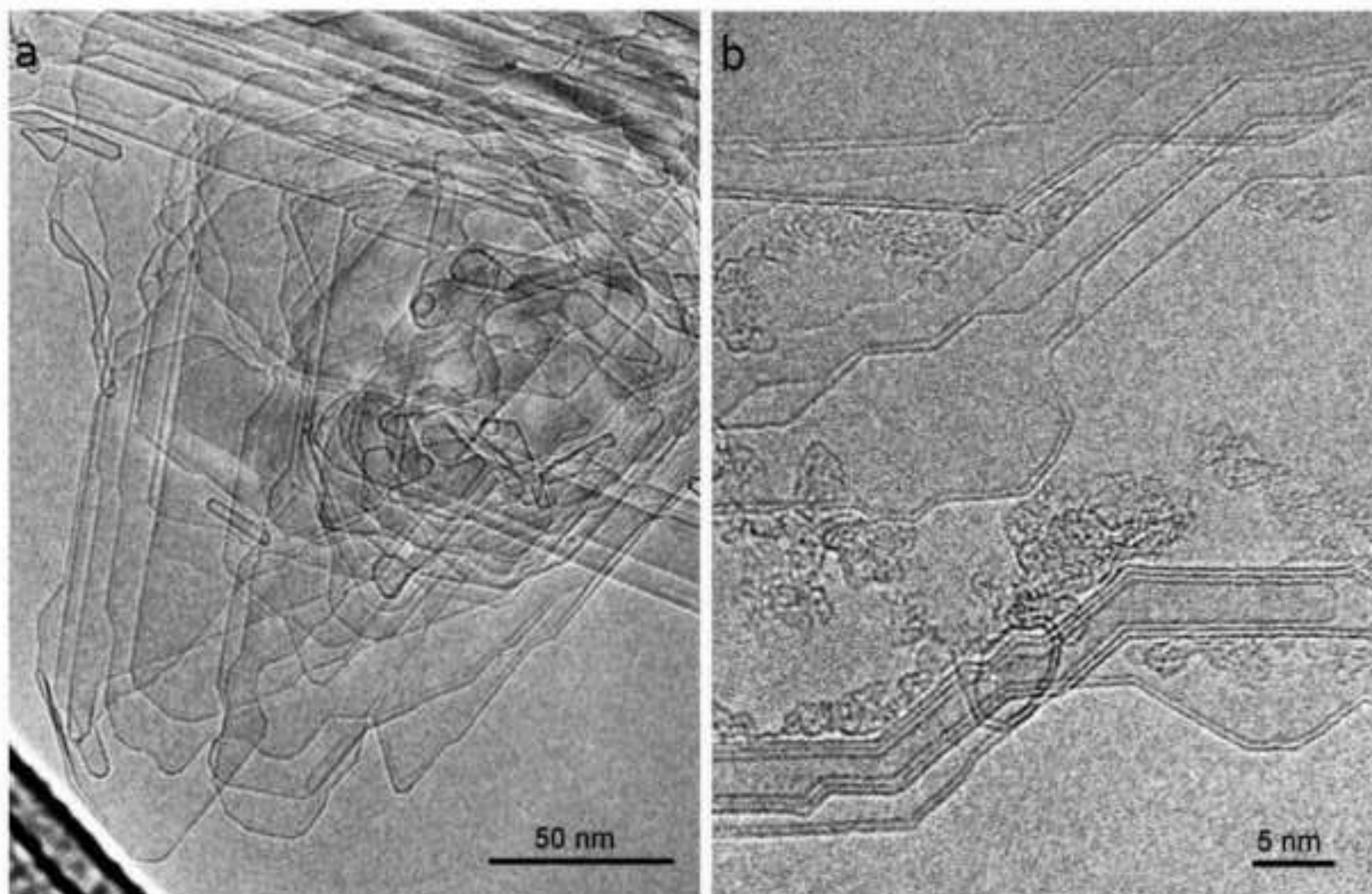


Fig. 2

Figure(s)

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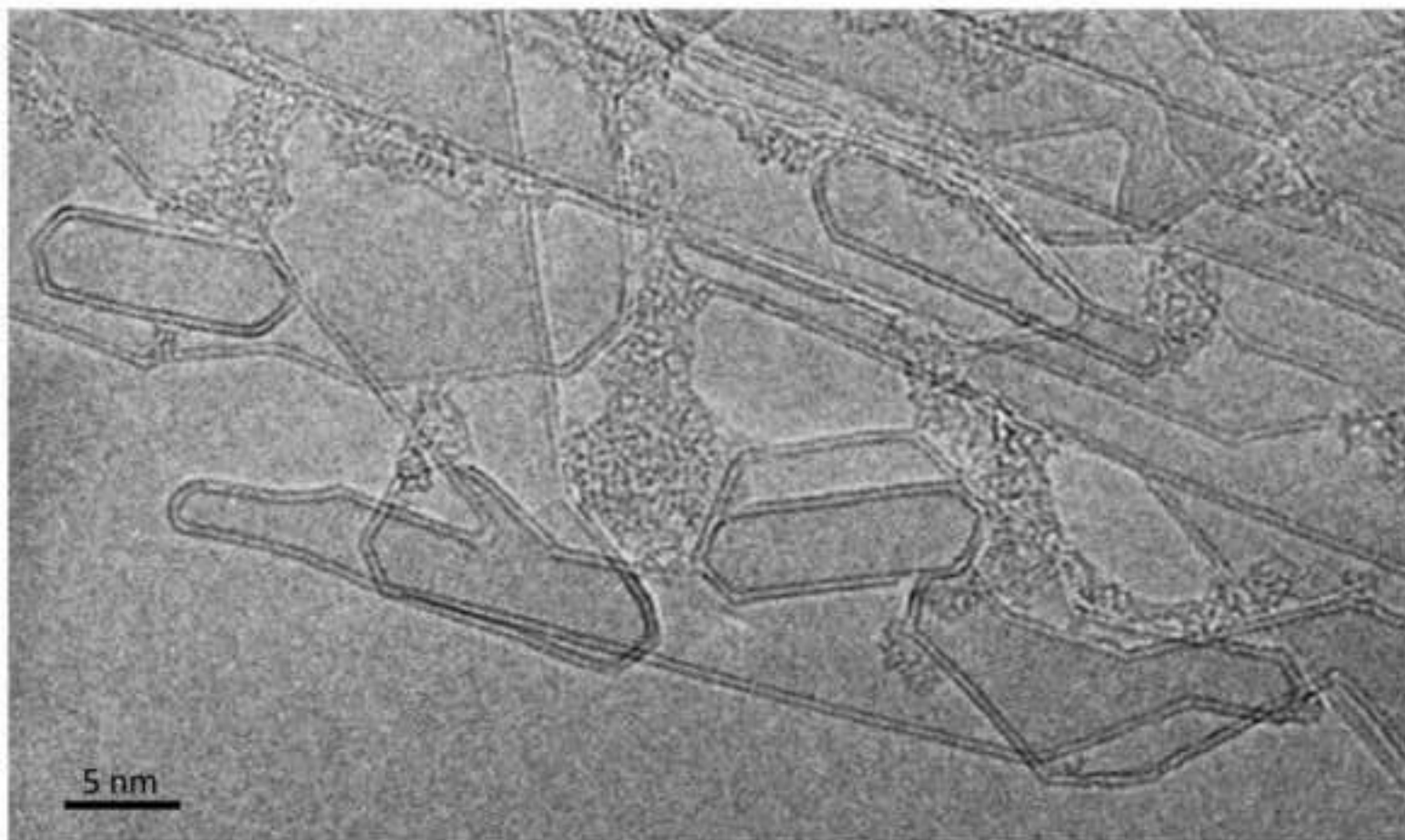


Fig. 3

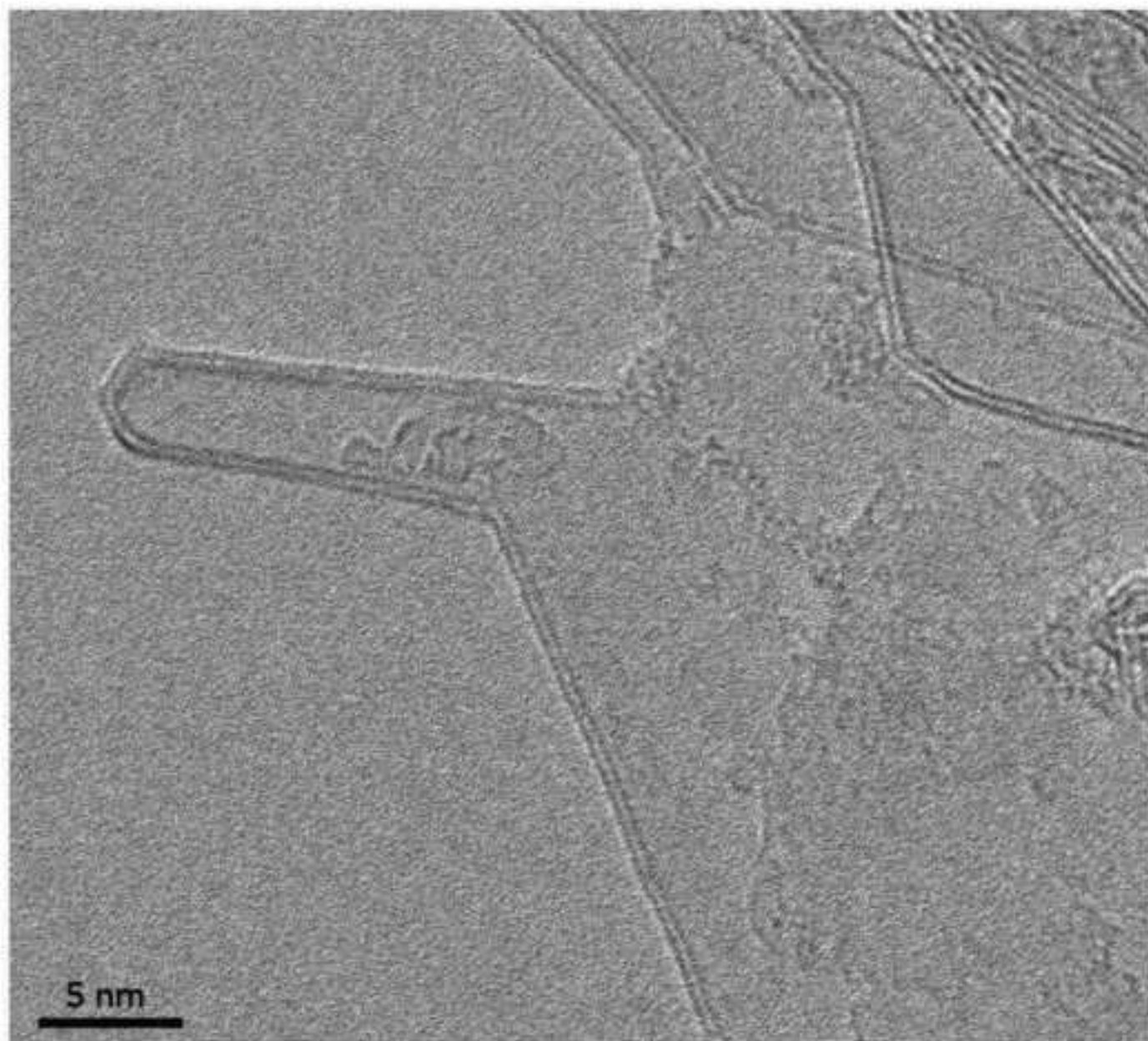


Fig. 4

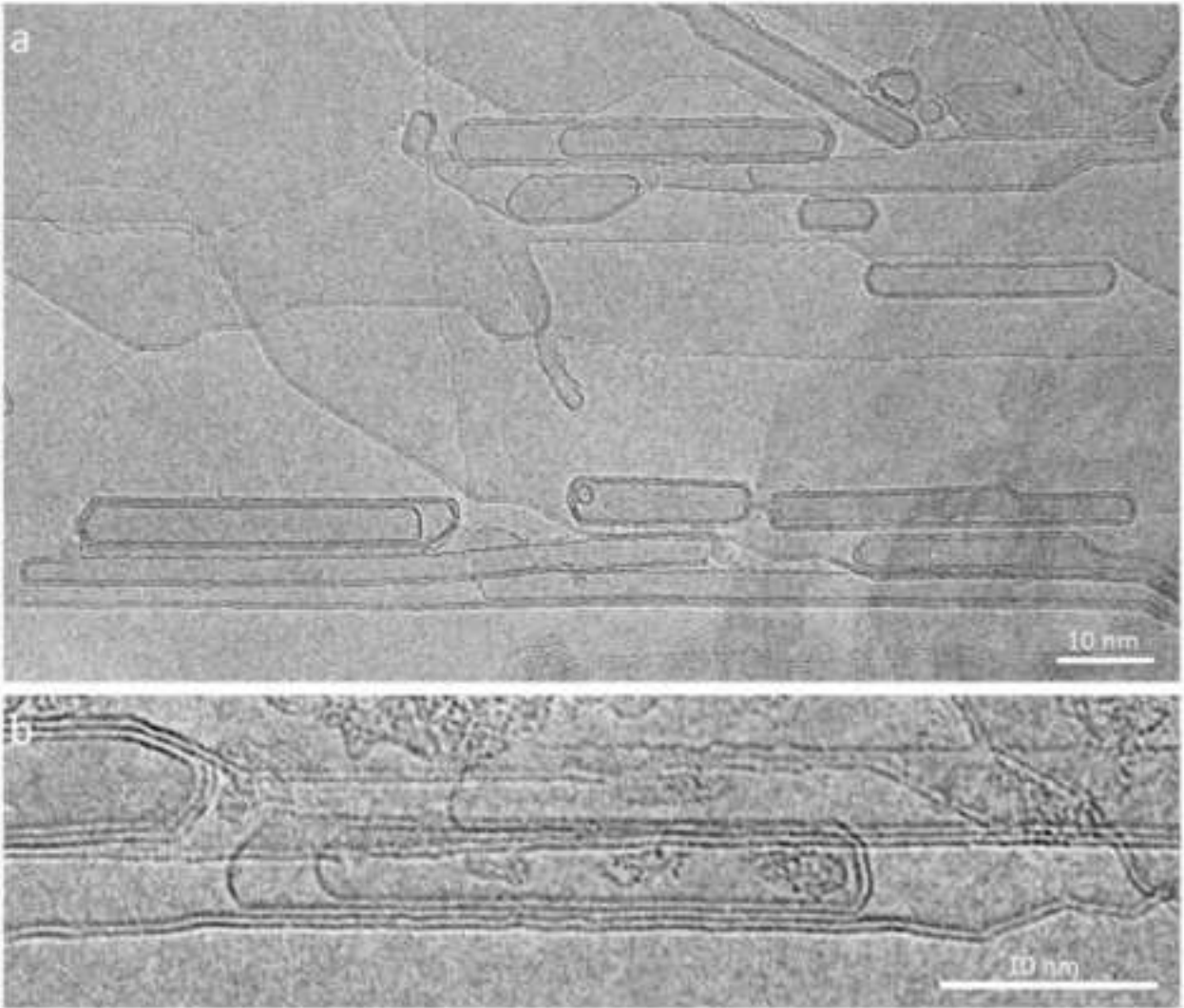


Fig 5

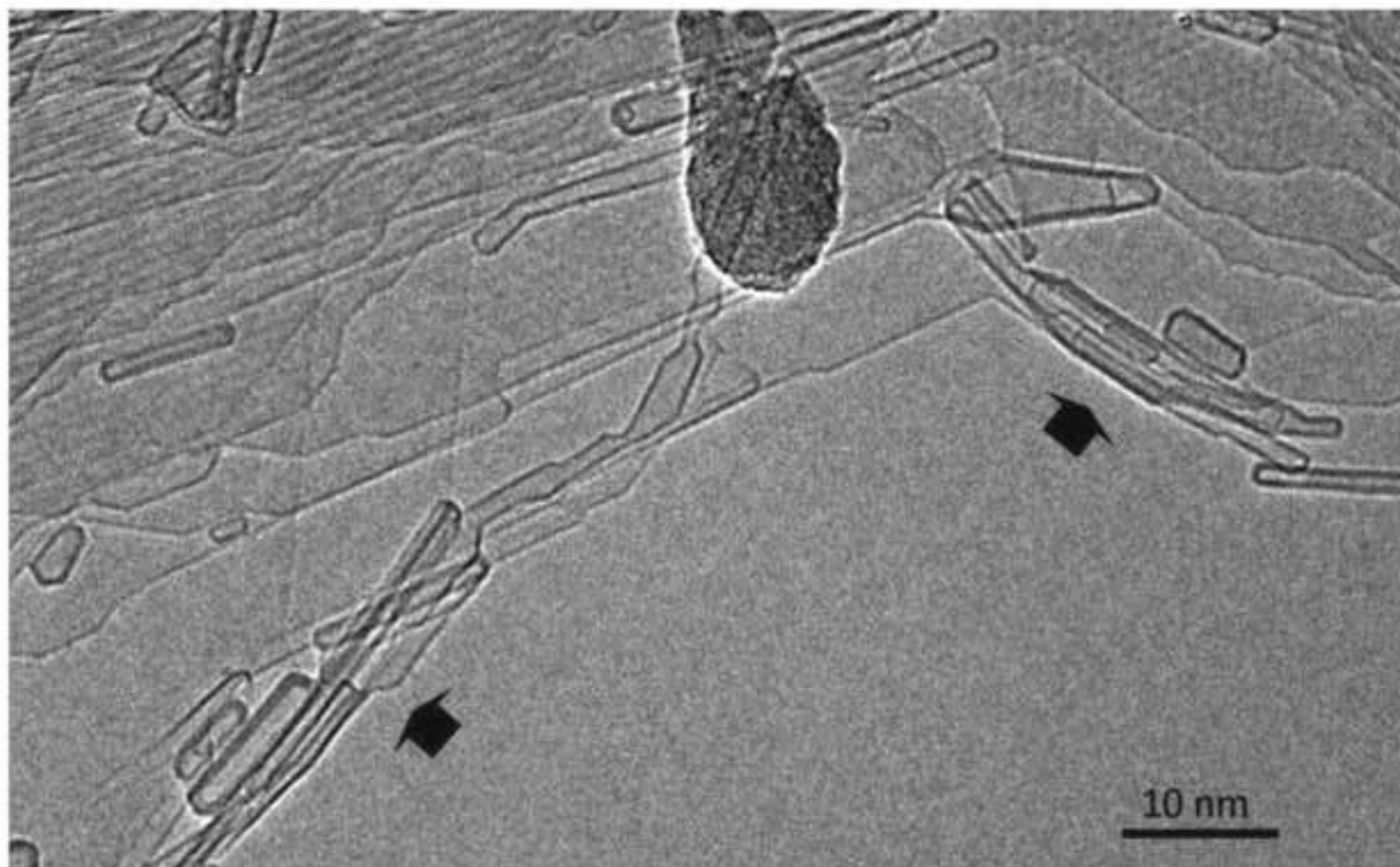
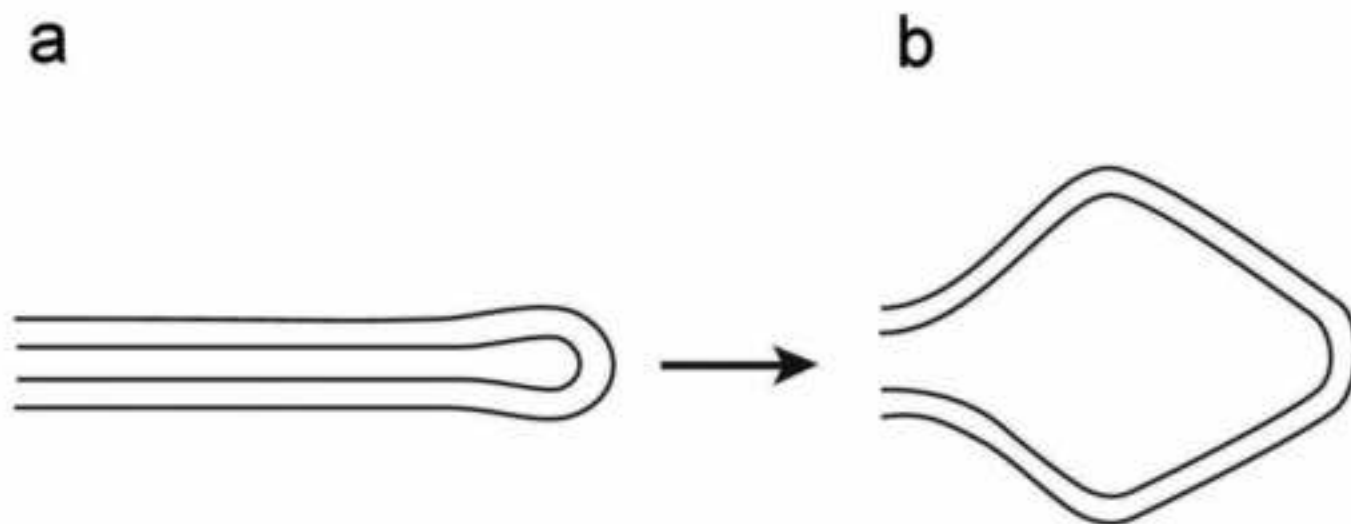
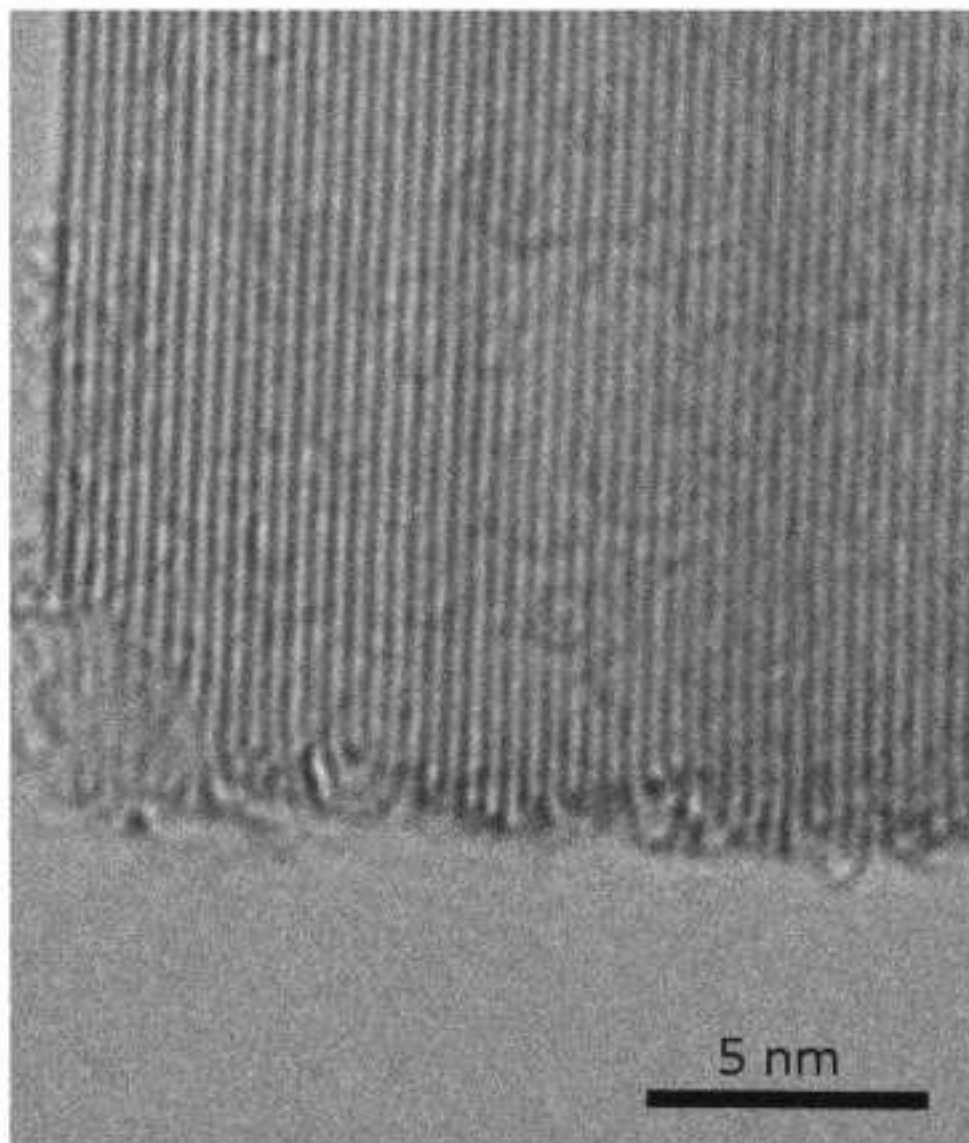
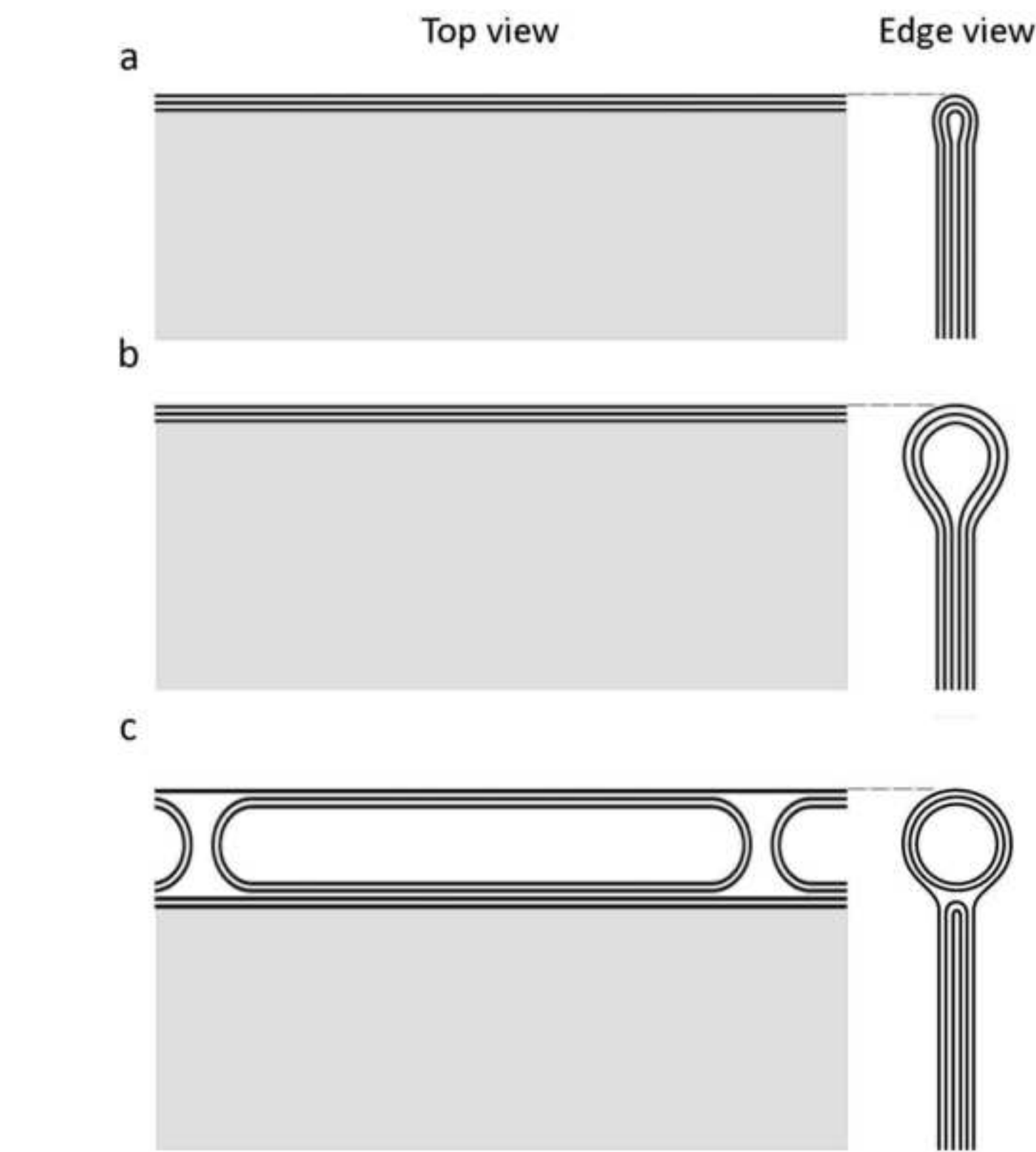


Fig. 6







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Response to further reviewer comments in email dated 22/05/2016

I do not feel that additional references in the Introduction are needed, as I discuss potential applications (with references) in the Discussion.

I have expanded the Discussion of scroll-like structures, and added the reference to Gass on p5.