Non-Graphitizing Carbon: Its Structure and Formation from Organic Precursors

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Abstract

Non-graphitizing carbon, or char, has been intensively studied for decades, but there is still no agreement about its detailed atomic structure. The first models for graphitizing and non-graphitizing carbons were proposed by Rosalind Franklin in the early 1950s, and while these are correct in a broad sense, they are incomplete. Subsequent models also fail to explain fully the structure of non-graphitizing carbons. The discovery of the fullerenes and related structures stimulated the present author and others to put forward models which incorporate non-hexagonal rings into hexagonally-bonded sp^2 carbon networks, creating a microporous structure made up of highly curved fragments. However, this model has not been universally accepted. This paper reviews the models that have been put forward for non-graphitizing carbon and outlines the evidence for a fullerene-like structure. This evidence comes from transmission electron microscopy, electron energy loss spectroscopy and Raman spectroscopy. Finally, the influence of precursor chemistry on the structure of graphitizing and non-graphitizing carbons is discussed. It is well established that carbonization of oxygen–containing precursors tends to produce non-graphitizing carbons. This may be explained by the fact that the removal of oxygen from a hexagonal carbon network can result in the formation of pentagonal carbon rings.

1. Introduction

In 1951, Rosalind Franklin demonstrated that carbons produced by the pyrolysis of organic materials fall into two distinct classes, graphitizing and non-graphitizing [1, 2]. Graphitizing carbons are soft and non-porous and, as the name suggests, can be transformed into crystalline graphite by heating to a temperature of 3000 °C. These include materials such as petroleum coke, pitch coke and coking coals. Non-graphitizing carbons tend to be hard, low density materials, with isotropic, microporous structures, which cannot be converted to graphite by heat-treatment at any temperature. They are otherwise known as "chars" or, more colloquially, "charcoal". Franklin showed that the chemical nature of the organic precursors tended to determine whether a graphitizing or non-graphitizing carbon

was produced by pyrolysis. Thus, in Franklin's words, "graphitizing carbons are formed, in general, from substances containing much hydrogen" while "non-graphitizing carbons are formed, in general, from substances containing little hydrogen or much oxygen". However, there were exceptions to this. For example, carbon derived from polyvinylidene chloride (PVDC), which contains no oxygen, is non-graphitizing.

Despite the huge amount of research carried out since the time of Franklin, there is still no universally accepted model for the structure of graphitizing and non-graphitizing carbons. The present author and others have argued that the difference between the two lies in the fact that non-graphitizing carbons contain non-hexagonal rings, mainly pentagons, while graphitizing carbons are made up largely of hexagons [3–8]. In other words, the non-graphitizing carbons (NGCs) have a structure related to that of the fullerenes. However, this idea has met with resistance from some quarters.

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The main aim of this review is to describe the fullerene-like model for non-graphitizing carbons and to review the experimental evidence in support of this model. The implications of the model for understanding the effect of precursor chemistry on graphitizability are discussed. Firstly, the structural models for graphitizing and non-graphitizing carbons that have been proposed since the time of Rosalind Franklin are reviewed.

2. Structural models of graphitizing and non-graphitizing carbons

The models which Franklin proposed in her 1951 paper are shown in Fig. 1. In these models, the basic units are small graphitic crystallites containing a few layer planes, which are joined together by cross-links. The non-graphitizing carbon consists of randomly ordered crystallites, held together by residual cross-links and van der Waals forces, as in Fig. 1(a). During high-temperature treatment, even though these cross-links may be broken, the activation energy for the motion of entire crystallites, required for achieving the structure of graphite, is too high and graphite is not formed.

On the other hand, the structural units in a graphitizing carbon are approximately parallel to each other, as in Fig. 1(b), and the transformation of such a structure into crystalline graphite would be expected to be relatively facile. While Franklin's ideas on graphitizing and non-graphitizing carbons may be broadly correct, they are in some regards incomplete. For example, the nature of the cross-links between the graphitic fragments is not specified, so the reasons for the sharply differing properties of graphitizing and non-graphitizing carbons is not explained.

The advent of high resolution transmission electron microscopy (HRTEM) in the late 1960s enabled the structure of non-graphitizing carbons to be imaged directly. In a typical study, Ban, Crawford and Marsh [9] examined carbons prepared from polyvinylidene chloride (PVDC) following heat treatments at temperatures in the range 530–2700 °C . Images of these carbons apparently showed the presence of curved and twisted graphite sheets, typically two or three layer planes thick, enclosing voids. These images led Ban et al. to suggest that heat treated NGCs have a ribbon-like structure. This ribbon-like model is rather similar to an earlier model of glassy carbon proposed by Jenkins and Kawamura [10]. However, models of this kind, which are intended to represent the struc-
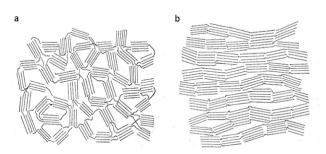

Fig. 1. Franklin's representations of (a) non-graphitizing and (b) graphitizing carbons [1].

ture of non-graphitizing carbons following high temperature heat treatment, have serious weaknesses. Such models consist of curved and twisted graphene sheets enclosing irregularly-shaped pores. However, graphene sheets are known to be highly flexible, and would therefore be expected to become ever more closely folded together at high temperatures, in order to reduce surface energy. Indeed, tightly folded graphene sheets are quite frequently seen in carbons which have been exposed to extreme conditions [11–13]. Thus, the ribbon-like structures would be unlikely to be stable at very high temperatures.

Oberlin and colleagues have also carried out detailed analyses of HRTEM images of graphitizing and non-graphitizing carbons [14–17]. Their view is that "all carbonaceous materials are initially made of similar elemental bricks arranged differently relative to each other". They suggest that "The elemental unit or basic structural unit (BSU) is made of planar aromatic structures consisting of less than 10–20 rings and piled up more or less in parallel by two to four". Cross-linking between the BSUs in non-graphitizing carbons prevents graphitization. This is a broadly similar view to that put forward by Franklin in her original 1951 paper, but Oberlin et al. have considered the nature of the cross-links in more detail, and suggest that they may involve either covalent bonds (e.g. ether functions) or polar intermolecular interactions [16].

All of the models discussed so far have been based on the assumption that the atoms in non-graphitizing carbon are bonded in hexagonal rings. However, the discovery of the fullerenes [18, 19] and subsequently of related structures such as carbon nanotubes [20] has given us a new perspective on solid carbon structures. We now know that carbons containing pentagonal rings, as well as other non-six-membered rings, among the hexagonal sp^2 carbon network, can be highly stable. This has prompted a number of groups to
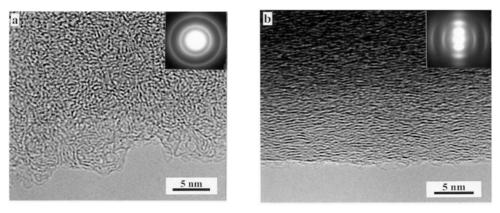
Fig. 2. (a) High resolution TEM image of carbon prepared by pyrolysis of sucrose in N$_2$ at 1000 °C; (b) carbon prepared by pyrolysis of anthracene at 1000 °C. Insets show selected area diffraction patterns [5].

take a fresh look at well-known forms of carbon, to see whether any evidence could be found for the presence of fullerene-like structures. The first studies of this kind were carried by the present author and S.C. Tsang in 1997 [3]. In this work, some non-graphitizing carbons were examined using TEM before and after heat treatments at very high temperatures (up to 2600 °C). For comparison, graphitizing carbons treated in a similar way were also examined. Typical TEM micrographs of non-graphitizing and graphitizing carbons prepared at 1000 °C are shown in Fig. 2. The insets show diffraction patterns recorded from areas approximately 0.25 μm in diameter. The image of the non-graphitizing carbon shows the structure to be disordered and isotropic, consisting of tightly curled single carbon layers, with no obvious graphitization. The diffraction pattern shows symmetrical rings, confirming the isotropic structure. The appearance of the graphitizing carbon, on the other hand, approximates much more closely to that of graphite. In this case, the structure contains small, approximately flat carbon layers, packed tightly together with a high degree of alignment.

The fragments can be considered as rather imperfect graphene sheets. The diffraction pattern for the graphitizing carbon consists of arcs rather than symmetrical rings, confirming that the layers are preferentially aligned along a particular direction. The bright, narrow arcs in this pattern correspond to the interlayer {002} spacings, while the other reflections appear as broader, less intense arcs.

Micrographs showing the effect of high-temperature heat treatments on the structure of non-graphitizing and graphitizing carbons are shown in Fig. 3 (note that the magnification here is much lower than for Fig. 2). In the case of the non-graphitizing carbon, heating at 2300 °C in an inert atmosphere produces the disordered, porous material shown in Fig. 3(a). This structure is made up of curved and faceted graphitic layer planes, typically 1–2 nm thick and 5–15 nm in length, enclosing randomly shaped pores. A few somewhat larger graphite crystallites are present, but there is no macroscopic graphitization. In contrast, heat treatment of the anthracene-derived carbon produces large crystals of highly ordered graphite, as shown in Fig. 3(b). More detailed analysis
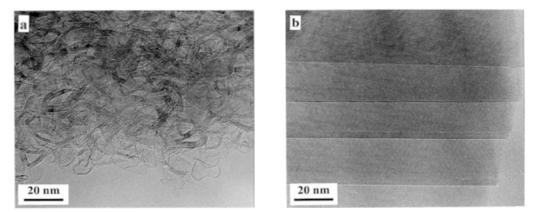

Fig. 3. Micrographs of (a) sucrose carbon and (b) anthracene carbon following heat treatment at 2300 °C [6].

of the heat-treated NGCs showed that they often contained completely closed nanoparticles. These particles were usually faceted, and often hexagonal or pentagonal in shape. The closed nature of the nanoparticles and their hexagonal or pentagonal shapes strongly suggested that the particles have fullerene-like structures. Much more recent work by Abrahamson et al. has shown that sucrose char heated rapidly to 2600 °C using a CO_2 laser contains completely closed shell nanoparticles, which could be opened by further heat-treatment [21].

The observation of fullerene-related nanoparticles in the heat-treated carbons suggests that the original, freshly prepared carbons may also have had fullerene-related structures. This prompted the present author and colleagues to propose a model for the structure of non-graphitizing carbons which consists of discrete fragments of curved carbon sheets, in which pentagons and heptagons are dispersed randomly throughout networks of hexagons, as shown in Fig. 4.

The development of aberration-corrected TEMs in recent years has enabled the atomic structures of carbon materials to be imaged directly [22, 23].
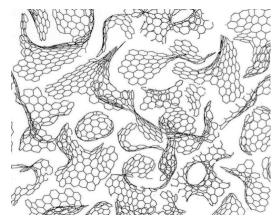

Fig. 4. Schematic illustration of a model for the structure of non-graphitizing carbons based on fullerene-like elements [7].

Much of the work in this area has focussed on carbon nanotubes and graphene, but a few studies of microporous carbons have been carried out. In the first of these, the present author, with Z. Liu and K. Suenaga described aberration-corrected TEM studies of a commercial activated carbon, Norit GSX [24]. Obtaining atomic resolution images of the fresh carbon proved to be extremely challenging,
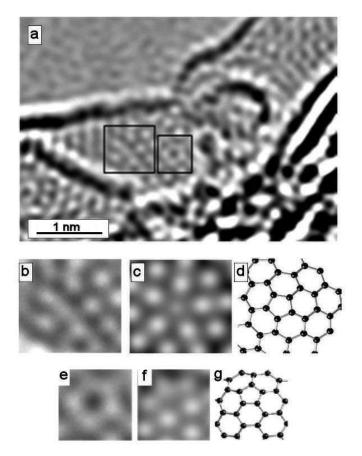

Fig. 5. (a) Aberration-corrected micrograph of activated carbon heated to 2000 °C; (b) Enlarged region showing pentagonal arrangement of spots; (c) Simulated image of structure shown in (d); (e) Second region showing pentagonal arrangement; (f) Simulated image of structure shown in (g) [24].

and the images which were recorded were difficult to interpret. Much better quality images could be obtained from carbon samples which had been heated at high temperature, to increase the crystallinity. An image from a carbon sample which had been heated in Ar to 2000 °C is shown in Fig. 5(a). Here, there is a clear evidence for the presence of five-membered rings. The area enlarged in Fig. 5(b) shows an arrangement of five bright spots surrounding a central spot. A good match was obtained with the simulated image in Fig. 5(c), which was obtained from the structure in Fig. 5(d) using a standard multi-slice procedure. Here, the pentagon is oriented approximately parallel to the plane of the image. A second area which contains a pentagonal structure is shown in Fig. 5(e). In this case, the central pentagonal ring is not visible, apparently because the ring is tilted away from the plane of the image. Support for this comes from the reasonable match which can be seen between the image and the simulated image in Fig. 5(f), obtained from the structure in Fig. 5(g). Images of this kind provide convincing evidence for the presence of pentagonal carbon rings in the heat-treated carbon.

Aberration-corrected TEM images of "fresh" microporous carbons have been reported by Guo et al. [25]. The structures they report are slightly different from those shown in Fig. 5 in that groups of pentagonal and heptagonal carbon rings are present, rather than isolated pentagons. This prompted the authors to propose a model for microporous carbon in which non-hexagonal rings produce crumpled graphene sheets, which expands the average interplanar spacing and creates slit-like nanopores. Further aberration-corrected imaging would be of great value in determining whether this model, or a model like that in Fig. 4, is closer to the true structure.

In addition to the TEM studies, a wide range of other techniques have produced evidence for the presence of non-hexagonal rings in microporous carbons. These include electron energy loss spectroscopy (EELS) [26], Raman spectroscopy [27–30] and NMR [31]. Theoretical work on sp^2-bonded microporous carbon has also provided support for a fullerene-related structure. Powles, Marks and Lau have described a comprehensive molecular-dynamics study of the self-assembly of carbon nanostructures [32]. The precursor for these simulations was highly disordered amorphous carbon, which was generated by rapid quenching of an equilibrated liquid sample. It was found that, under certain conditions, annealing the amorphous carbon at high temperature could lead to highly curved sp^2 sheet structures containing pentagons and heptagons which were very similar to the model shown in Fig. 4. Fullerene-like models for microporous carbon have been used by Terzyk and colleagues to predict the adsorptive properties of microporous carbons, and in many cases a good agreement with experimental results has been found [33–36].

3. The effect of precursor chemistry on graphitizability

As noted in the Introduction, Franklin showed that the chemical nature of the organic precursors tended to determine whether a graphitizing or non-graphitizing carbon was produced by pyrolysis, and this has been confirmed in many subsequent studies. Thus carbonization of oxygen–containing precursors tends to produce non-graphitizing carbons, while carbonization of precursors containing significant amounts of hydrogen usually produces graphitizing carbons. It has also been shown that it is possible to convert graphitizable polymeric materials into non-graphitizing carbons by oxidizing the starting materials in the early stages of carbonization [37]. The effect of heteroatoms other than oxygen tends to be more complicated. Thus, some sulphur-containing precursors give non-graphitizing carbons while others give graphitizing [15]. The differing behaviour of the two chlorine-containing polymers which were studied by Franklin, is interesting. Polyvinylidene chloride $(C_2H_2Cl_2)_n$ gives a non-graphitizing carbon, while polyvinyl chloride $(C_2H_3Cl)_n$, gives a graphitizing carbon. Franklin pointed out that PVDC contains only enough hydrogen to combine with the chlorine to form HCl during decomposition, leaving pure carbon, while PVC, with more hydrogen and less chlorine, decomposes into a pitch-like substance rich in hydrocarbons. It seems that the precursors of graphitizing carbons all pass through a liquid stage upon heat treatment, although whether the physical or chemical properties of the precursors are more important in determining their graphitizability is not clear. The puzzle of why precursors containing oxygen and other heteroatoms produce non-graphitizing carbon has also not been satisfactorily answered, and this is the question that will be considered in this section.

If we once again assume that the "fullerene" model for the structure of non-graphitizing carbon is correct, i.e. that these carbons contain
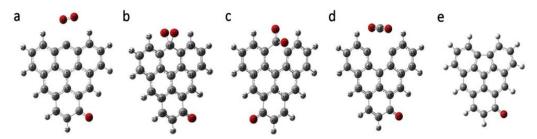
Fig. 6. Structures selected from computer simulation by Radovic et al. of the reaction between O_2 and the zig-zag edge of a char, to produce CO_2 [44].

pentagons and other non-six-membered rings as well as hexagons, then the question becomes "why do precursors containing heteroatoms produce non-hexagonal rings?". McDonald-Wharry et al. have discussed this topic in a recent review [38]. In particular, they consider the mechanisms whereby the removal of oxygen from O-containing precursors might result in the formation of pentagons. They cite work by Homann on fullerene production during the incomplete combustion of hydrocarbons [39]. Homann suggested that the removal of oxygen from partially oxidized PAH-like structures in the form of carbon monoxide could cause the formation of pentagonal rings. It is possible that similar a pentagon formation mechanism might occur during the carbonization of oxygen-containing precursors. McDonald-Wharry et al. have also suggested that there are parallels between the carbonization of chars and the reduction of graphene oxides [40, 41]. It has been shown by aberration-corrected TEM that reduced graphene oxide contains pentagonal and heptagonal rings [42, 43]. In some cases these defects are configured in a way which maintains a planar structure, while in other cases they produce curvature or wrinkling of the graphene. While there are clearly considerable differences between reduced graphene oxides and chars, the idea that pentagon formation in both materials might involve a similar process is worth further study.

Work by Radovic et al. on the oxidation of chars also demonstrates that the removal of oxygen from a hexagonal carbon network can result in the formation of pentagons [44]. Figure 6, taken from their work, shows the proposed mechanism for the reaction of O_2 and the zig-zag edge of a char, to produce CO_2. It can be seen that the final structure contains a pentagon. Although Radovic et al. are modelling carbon oxidation rather than the carbonization of an oxygen–containing precursor, it is possible that a similar mechanism might be involved in both processes.

There seems to be little evidence that heteroatoms other than oxygen can promote pentagon formation, but McDonald-Wharry et al. draw attention to work by Nieto-Marquez et al. on the production of carbon "nanospheres" by pyrolysis of benzene, aniline and nitrobenzene [45]. These authors showed that carbon nanostructures produced from the nitrogen-containing precursors displayed greater curvature, and they suggested that this was because the presence of nitrogen facilitated pentagon formation. Similarly, recent work by Abrahamson and Vander Wal has shown that annealing of sulphur-doped synthetic soot can result in curvature of the carbon structure, which may be due to the formation of non-hexagonal carbon rings [46].

4. Conclusion

This paper began with a brief review of structural models for non-graphitizing carbons, beginning with the pioneering work of Rosalind Franklin. None of these models was entirely successful in explain the properties of non-graphitizing carbons, such as their hardness and extreme resistance to graphitization. A more recent model was then described, which assumes that the structure is made up of curved carbon sheets, in which pentagons and heptagons are dispersed randomly throughout networks of hexagons. Research on fullerene-related carbons has shown that non-hexagonal rings can be extremely stable, and could therefore be responsible for the resistance of NGCs to graphitization and their hardness. As mentioned above, this model is gaining support from experimental studies. Moreover, theoretical work [e.g. 33] has also shown that fullerene-like models can replicate experimentally observed pore size distributions and adsorption isotherms. The "fullerene" model may also help us to understand the effect of precursor chemistry on graphitizability. As discussed, there is evidence from work by a number of groups that the removal of oxygen from O-containing precursors can result in the formation of pentagons,

thus possibly explaining why such precursors tend to form non-graphitizing carbons. Modelling work on the carbonization of O-containing carbonaceous materials would be helpful in establishing whether these ideas are correct.

Acknowledgement

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