High-resolution electron microscopy of a microporous carbon

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Abstract

The structure of a microporous carbon prepared by the carbonization of sucrose was examined using high-resolution electron microscopy. It was found to be disordered and isotropic and primarily made up of tightly curved individual carbon layers, enclosing pores typically about 1 nm in size. Completely closed carbon particles were also present. These observations suggest that the carbon may have a fullerene-related structure, in which pentagons and heptagons are distributed randomly throughout a hexagonal network, producing continuous curvature.

§ 1. Introduction

Microporous carbons can be prepared by the pyrolysis of a wide variety of materials, ranging from synthetic polymers to sugar. When 'activated' by mild oxidation with a gas or by chemical processing, these carbons can have enormously high internal surface areas, and they are widely used as adsorbents for the purification of air or water (Jankowska *et al.* 1991). Despite much research, however, the detailed structure of microporous carbons at the atomic level is still poorly understood. Some researchers have suggested that sp^3-bonded carbon may be present (for example Ergun and Tiensuu (1959)), but detailed analysis of neutron scattering data has suggested that the amount of tetrahedrally bonded atoms in microporous carbons is negligible (Burian *et al.* 1998). Other workers have interpreted high-resolution electron micrographs as implying that microporous carbons have a ribbon-like structure (for example Ban *et al.* (1975)). However, such models do not seem to explain fully the characteristic properties of these carbons, such as their porosity, hardness and resistance to graphitization (Harris 1997). Recently, it has been suggested that microporous, non-graphitizing carbons might have a fullerene-related structure made up of fragments in which pentagonal and heptagonal rings are distributed randomly throughout a hexagonal network (Harris and Tsang 1997). The aim of the present study is to examine a typical microporous carbon using high-resolution

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electron microscopy (HREM), to see whether there is evidence to support the idea that fullerene-related structures are present.

§ 2. EXPERIMENTAL TECHNIQUES

The microporous carbon studied here was prepared by the carbonization of sucrose in flowing argon. The sample preparation consisted of three steps. First, a char was prepared by heating sucrose at 230°C and then at 400°C. The obtained material was then ground to produce a grain size of approximately 1 mm. This was heated to 1000°C and held at this temperature for 30 min. The product of this treatment was a carbon which contained less than 1% non-carbon material. For comparison, a graphitizing carbon was also prepared, by the carbonization of anthracene under similar conditions at 1000°C.

Samples were prepared for transmission electron microscopy by grinding gently and depositing on to 'lacey' carbon support films. The microscopes employed were a Philips CM20 operated at 200 kV and a JEOL 4000FX operated at 400 kV.

§ 3. RESULTS AND DISCUSSION

Figure 1 (*a*) shows a typical high-resolution electron micrograph of the microporous carbon prepared from sucrose, with an inset showing a diffraction pattern recorded from an area approximately 0.25 µm in diameter. The image shows the structure to be disordered and isotropic, with little obvious graphitization. The diffraction pattern shows symmetrical rings, confirming the isotropic structure. These observations are consistent with neutron diffraction studies of activated carbons, which have shown that graphite interlayer correlations are completely absent (Burian *et al.* 1998).

The graphitizing carbon has a structure in which the carbon layers are clearly aligned along a preferred direction and are packed closely together. This can be seen in the image shown in figure 1 (*b*). It is notable that the surface of this carbon is relatively flat, in contrast with the irregular surface of the microporous carbon, as a result of the much closer packing of the graphene layers. 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 {0002} spacings, while the other reflections appear as broader, less intense arcs.

Many areas of the microporous carbon were too thick to enable structural information to be obtained. However, thin regions could often be found near the edges of particulates, and a large number of images of such regions were recorded. These images showed the microstructure to be made up of tightly curled carbon layers which often enclosed voids of the order of 1 nm in size. Figure 2 shows some examples. In figure 2 (*a*), the arrow indicates an onion-like structure in which concentric sheets are curled around a central cavity. Figure 2 (*b*) shows an individual, completely closed particle. Such structures were quite commonly observed but were rather difficult to photograph as they tended to be mobile in the electron beam. Figure 2 (*c*) shows a tightly curled carbon layer, with a second layer apparently forming around it.

As noted above, images of microporous carbons such as those shown in figure 1 (*a*) and figure 2 have traditionally been interpreted in terms of a structure made up of curled and twisted graphene ribbons. However, we believe that such an explanation is unlikely to be correct. Graphene ribbons have a natural tendency to lie flat
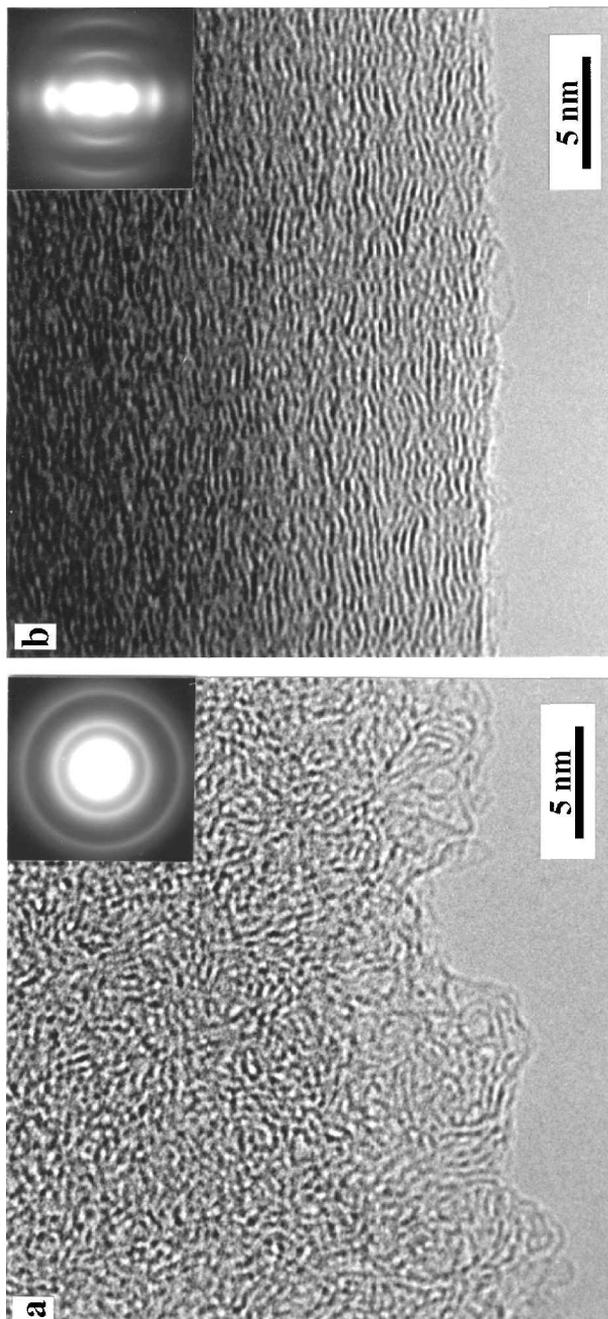
Figure 1. (*a*) High-resolution electron micrograph of carbon prepared by pyrolysis of sucrose in argon at 1000°C; (*b*) carbon prepared by pyrolysis of anthracene at 1000°C. The insets show selected-area diffraction patterns.
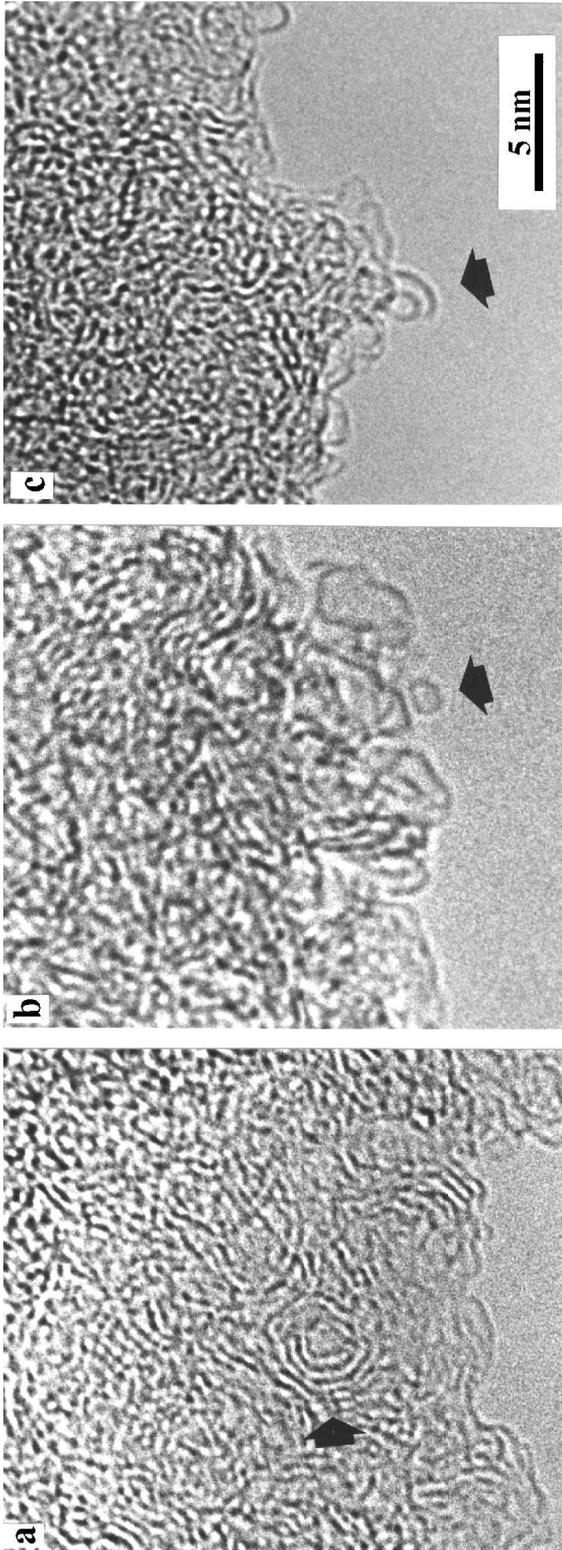
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Figure 2. Micrographs of sucrose carbon showing (*a*) a structure with concentric layers curving around central cavity and (*b*) a completely closed structure and (*c*) an individual carbon layer apparently curling around existing structure.
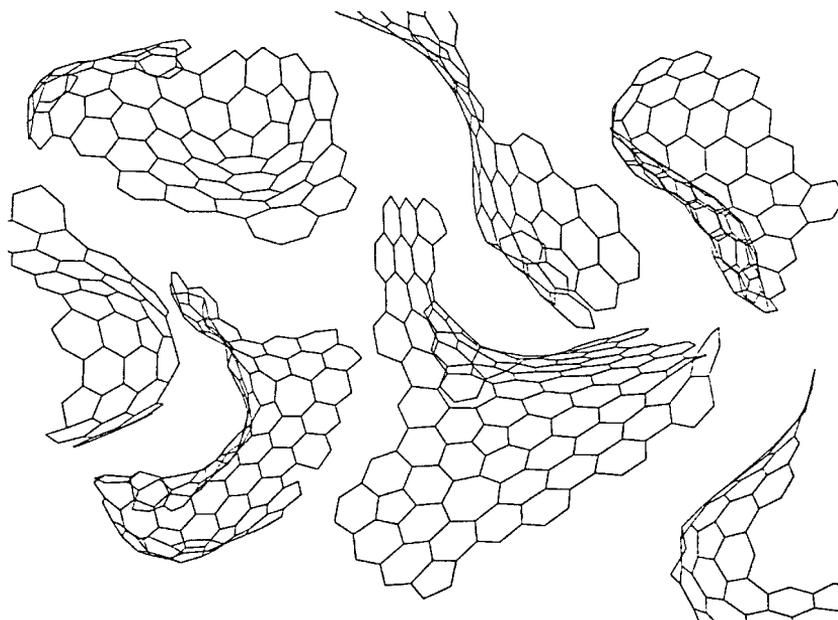
Figure 3. Illustration of a model for the structure of non-graphitizing carbons based on fullerene-like elements.

and pack closely together, as observed in the graphitizing carbon, rather than to curl and twist. At high temperatures, one would expect the ribbons to become ever more closely packed, in order to reduce their surface energy. Yet we know that microporous carbons can retain their exceptionally high surface areas at temperatures of up to 1000°C. It would seem much more likely that the curved and closed structures result from the presence of fullerene-like elements, in which both pentagons and heptagons are distributed randomly throughout a hexagonal network, to produce the observed curvature. A schematic illustration of the kind of structure we envisage for microporous carbons is shown in figure 3. This model has some similarities to the 'random schwarzite' network proposed by Townsend *et al.* (1992). However, it should be noted that the curvature in schwarzite structures is generally negative, because of the presence of carbon rings with more than six members. In our structure, the curvature results primarily from the presence of pentagons and so is mainly positive. Also, unlike the Townsend structure, our model consists of discrete fragments rather than a single continuous sheet.

§ 4. CONCLUSIONS

In previous studies, HREM has been used to examine non-graphitizing, microporous carbons which have been heated at temperatures of around 2500°C (Harris 1997, Harris and Tsang 1997). It was found that these carbons consisted largely of curved or faceted two- or three-layer carbon sheets enclosing voids typically 5–15 nm in size. Closed nanoparticles were commonly observed. It was concluded that the faceting and curvature were probably due to the presence of pentagons and other non-hexagonal rings. In the present study, a 'freshly prepared' microporous carbon, heated to only 1000°C, has been studied. In this case there is also evidence for

pentagons, since the structure contains many tightly curved individual carbon layers, including completely closed structures. The degree of curvature in the freshly prepared carbon suggests that pentagons are much more common than in the high-temperature annealed carbons.

There appears to be growing support for the idea that microporous carbons may contain fullerene-like elements. A recent neutron diffraction study by Petkov *et al.* (1999) has shown that non-hexagonal rings may be present in carbons produced by pyrolysis of poly(furfuryl alcohol), while a Japanese group has demonstrated that C_{60} can be extracted from commercial wood charcoals (Shibuya *et al.* 1999). It also seems likely that anthracitic coal, which has properties rather similar to those of a char, may have a fullerene-related microstructure, although there is at present no direct evidence to support this idea.

The question arises as to the origin of pentagons and other non-hexagonal rings in microporous carbons. Acharya *et al.* (1999) have recently attempted to model the structural evolution of a microporous carbon, beginning with flat graphene fragments containing approximately 34 atoms. They show that pentagons and heptagons are readily formed during the coalescence of these fragments, leading to a structure containing random curvature and nanoscale porosity. Further modelling exercises of this kind would be of great value.

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