Imaging the structure of activated carbon using aberration corrected TEM

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Abstract. The precise atomic structure of activated carbon is unknown, despite its commercial importance. Here we show that the structure of a commercial activated carbon can be imaged directly using aberration corrected transmission electron microscopy. Images are presented both of the as-produced carbon and of the carbon following heat- treatment at 2000°C. In the 2000°C carbon clear evidence is found for the presence of pentagonal rings, suggesting that the carbons have a fullerene-related structure.

1. Introduction

Activated carbon is used on a huge scale in gas and water purification, metal extraction, medicine and many other applications, but its atomic structure is unknown. Rosalind Franklin showed in the 1950s that carbons produced by the pyrolysis of organic materials fall into two classes, which she called graphitizing and non-graphitizing [1]. The kind of carbon from which activated carbon is derived is non-graphitizing, meaning that it cannot be transformed into crystalline graphite even at temperatures as high as 3000°C. Franklin put forward a model of non-graphitizing carbon based on small graphitic crystallites joined together by cross-links, but did not explain the nature of these links. A more recent suggestion [2 - 5] is that non-graphitizing carbon has a structure related to that of the fullerenes, which consists of curved fragments containing pentagons and other non-hexagonal rings in addition to hexagons, as shown in Fig. 1. Such a structure would explain the microporosity of the carbon, and many of its other properties. However, obtaining direct experimental support for this hypothesis is difficult. Both X-ray and neutron diffraction have been extensively applied to non-graphitizing carbons, and in some studies the data has been interpreted in terms of a structure containing non-hexagonal rings [6]. But definitive proof that the atoms are bonded in pentagonal or hexagonal rings cannot be obtained using diffraction methods. Until relatively recently, imaging the atomic structure of carbons using transmission electron microscopy would also have been impossible, as the resolution was greater than the C-C bond length (0.142 nm). However, the development of aberration correctors has improved the resolution of TEM to the point where the direct imaging of carbon networks becomes possible. Here we apply this technique to a commercial activated carbon, namely Norit GSX. In addition to the as-received carbon, samples heated in Ar to 2000°C are imaged.

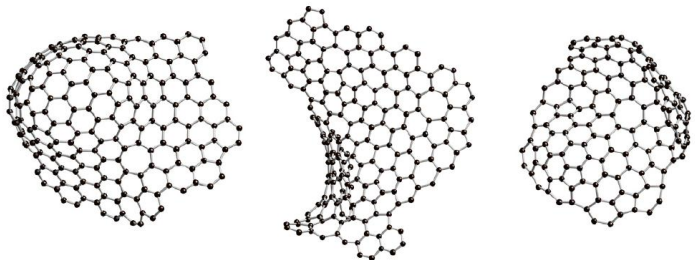

Figure 1: Illustration of curved carbon fragments containing pentagonal and heptagonal rings, in addition to hexagons.

2. Experimental Methods

Specimens were prepared for TEM by dispersing the carbon in iso-propyl alcohol, mixing ultrasonically and depositing onto holey carbon support films. Images showing the overall morphology of the carbons were recorded using the Reading University JEOL 2010 microscope, operated at 200kV. Atomic resolution imaging was carried out using the Tsukuba JEOL 2010F instrument, operated at 120kV. This has a post-specimen aberration corrector (CEOS), giving a point resolution of better than 0.14 nm at 120 kV. The Cs was set to a value in the range from 0.5 to 5 μm. Images were digitally recorded using a Gatan 894 CCD camera under a slightly under-focus condition (Δf = -1 to -6 nm). Image simulations were carried out using a standard multi-slice software package (Mactempas), with structural models prepared using the molecular modelling software DTMM, and appropriate values of Cs and defocus.

3. Results

Micrographs of typical areas of the as-received and 2000°C carbons are shown in Figs. 2 (a) and (b) respectively. The as-received carbon has a disordered and porous microstructure consisting mainly of tightly curled single carbon layers. In the 2000°C carbon, the structure is still disordered, but with larger pores, bounded by more perfect carbon layers.

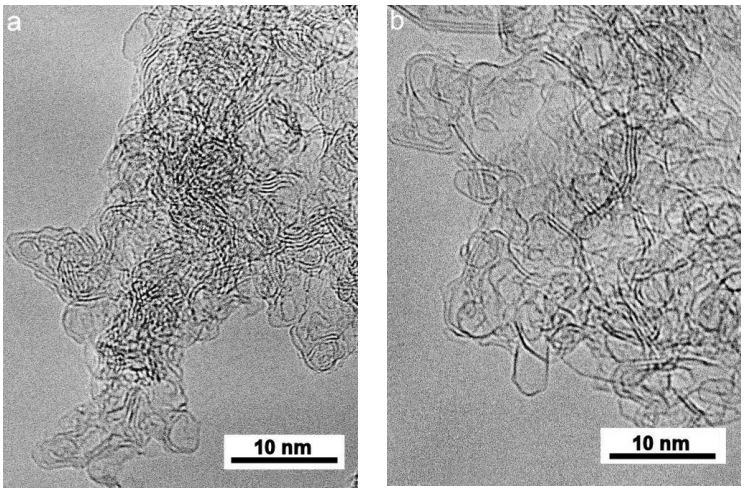

Figure 2: TEM micrographs showing general appearance of (a) fresh activated carbon, (b) activated carbon following heat treatment at 2000°C.

A typical atomic resolution image of the fresh carbon is shown in Fig. 3 (a). Here the bright spots represent the centres of the individual rings of carbon atoms. In most cases these bright spots form hexagonal arrangements, but pentagonal arrangements are also seen. In Fig. 3 (b) the bright spots have been highlighted, with the position of a possible pentagonal ring shown by a black dot. The images we have obtained of the fresh carbon are not yet of sufficient quality to justify comparisons with

simulations based on models of the structure. Nevertheless, our results demonstrate that atomic level imaging of this kind of highly disordered carbon is possible.

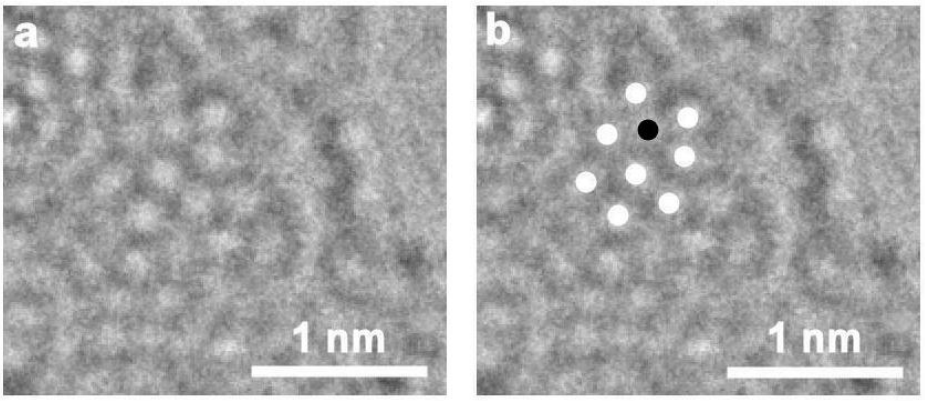

Figure 3: (a) Aberration-corrected HRTEM micrograph of fresh activated carbon, (b) same image, with white dots indicating hexagonal rings and black dot indicating possible pentagon.

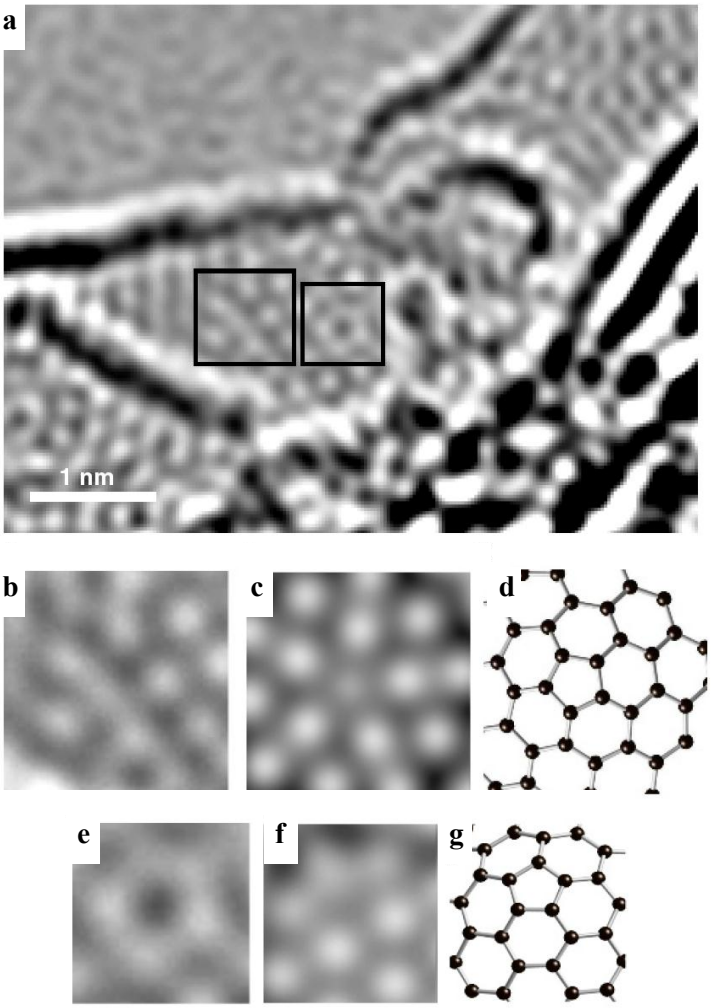

Figure 4: (a) Aberration-corrected micrograph of small area of the 2000°C-heated carbon. (b) Enlarged region showing pentagonal arrangement of spots. (c) Simulated image of structure shown in (d). (e) Second region showing pentagonal arrangement. (f) Simulated image of structure shown in (g).

Recording atomic resolution images of the 2000°C-heated carbon was considerably easier than for the as-prepared carbon, due to the greater degree of crystallinity. The carbon sheets in the heat-treated carbon were frequently just a single layer thick, and in such cases images could be obtained which showed the true atomic structure. In some areas there was clear evidence for the presence of five-membered rings. Figure 4 (a) shows a small region in which at least two such rings are apparently present. The area enlarged in Fig. 4 (b) shows an arrangement of 5 bright spots surrounding a central spot. A good match was obtained with the simulated image in Fig. 4 (c), which was obtained from the structure in Fig. 4 (d). 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. 4 (e). In this case the central pentagonal ring is not visible, and we believe this is 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. 4 (f), obtained from the structure in Fig. 4 (g). We recognise that the agreement between the images and simulations shown here is not exact, but this is to be expected since we are not dealing with perfect crystalline structures, but with disordered materials. Taking this into account, we believe that the agreement is sufficiently good to provide convincing evidence for the presence of pentagonal carbon rings.

4. Discussion

We have shown here that aberration-corrected TEM can be used to image the atomic structure of a conventional carbon material, specifically the commercial activated carbon Norit GSX. Images of the fresh carbon contained evidence of hexagonal rings, and possibly non-hexagonal ones, but were difficult to interpret due to the highly disordered structure. The 2000°C-heated carbon contained larger networks which were much more readily imaged, and showed clear evidence of pentagonal rings. Our results therefore support the idea, put forward more than ten years ago [2, 3] that this type of carbon has a fullerene-related structure. The idea that microporous carbons have a fullerene-like structure has important implications for the modelling of adsorption on such carbons. Traditionally, such modelling exercises have utilised structural models derived from graphite, in which all the atoms are in hexagonal rings. The carbon pores are then assumed to have a slit-like shape, confined by parallel planes. If the fullerene-like models are correct, these ideas may have to be modified. Indeed, theoretical studies have already been carried out which show that a model structure containing fullerene-related elements provides a better basis for understanding adsorption on activated carbon than the traditional models [e.g. 7, 8]. A fuller description of the present work has been published [9].

Acknowledgement

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