

# *Fullerene-like models for microporous carbon: a review*

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**Fullerene-like models for microporous carbon: A review**

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## Abstract

Microporous carbons are important in a wide variety of applications, ranging from pollution control to supercapacitors, yet their structure at the molecular level is poorly understood. Over the years, many structural models have been put forward, but none have been entirely satisfactory in explaining the properties of the carbons. The discovery of fullerenes and fullerene-related structures such as carbon nanotubes gave us a new perspective on the structure of solid carbon, and in 1997 it was suggested that microporous carbon may have a structure related to that of the fullerenes. Recently, evidence in support of such a structure has been obtained using aberration-corrected transmission electron microscopy, electron energy loss spectroscopy and other techniques. This article describes the development of ideas about the structure of microporous carbon, and reviews the experimental evidence for a fullerene-related structure. Theoretical models of the structural evolution of microporous carbon are summarised, and the use of fullerene-like models to predict the adsorptive properties of microporous carbons are reviewed.

**Keywords:** Microporous carbon, fullerenes, transmission electron microscopy, adsorption

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### 1. Introduction

The adsorptive properties of charcoal have been known for thousands of years. Egyptian papyri from 1500BC record the application of charcoal to adsorb odorous vapours from putrefying wounds, while Hindu documents from 450 BC refer to the use of sand and charcoal filters for the purification of drinking water [1]. In the 18th century, charcoal began to be used industrially for the decolourization of sugar syrups, while in the First World War the deployment of poisonous gases created an urgent need for adsorbent carbons suitable for use in respirators. Today, activated microporous carbon is used on an enormous scale for the purification of air and water [2,3]. It is still used widely in respirators, as well as in air-conditioning systems and in

1 the clean-up of waste gases from industry. In the liquid-phase, its largest  
2 single application is the removal of organic contaminants from drinking water.  
3  
4 Many water companies in Europe and the USA now filter all domestic supplies  
5 through granular activated carbon filters, and household water filters  
6  
7 containing activated carbon are also in widespread use. Other applications  
8  
9 include decontamination of groundwaters and control of automobile  
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11 emissions. Microporous carbon is also an important support material in  
12  
13 heterogeneous catalysis, and is used in lithium ion batteries and  
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15 supercapacitors. As a result of its commercial importance, charcoal has been  
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17 the subject of a huge amount of research in both industrial and academic  
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19 laboratories. Despite this, many important questions remain, not least about  
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21 its detailed atomic structure.  
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31 The primary aim of this article is to discuss the idea, first put forward by the  
32 present author and S.C. Tsang in 1997 [4,5], that charcoal, or char, has a  
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34 structure related to that of the fullerenes. In order to put this in context, a brief  
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36 outline of earlier work in the field is included. The article begins with a brief  
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38 description of the characteristics of graphitizing and non-graphitizing carbons,  
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40 and highlights the work of Rosalind Franklin in establishing the distinction  
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42 between these two forms of carbon. Some of the structural models which  
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44 have been put forward for non-graphitizing carbons are then discussed,  
45  
46 beginning with Franklin's original models, which were based on cross-linked  
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48 graphitic domains. Subsequent workers suggested that  $sp^3$ -bonded carbon  
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50 atoms might be present in the cross-links, while later workers interpreted  
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52 transmission electron microscopy (TEM) images of microporous carbon in  
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terms of a ribbon-like structure. The studies which led to the proposal of the fullerene-related model are then outlined, and experimental support for this structure is discussed. The strongest experimental support comes from studies carried out in the past four years using aberration-corrected TEM and electron energy loss spectroscopy (EELS). Both techniques provide evidence for the presence of pentagonal carbon rings in microporous carbon.

In the subsequent section, some attempts to model the structural evolution of microporous carbon are reviewed. It is notable that in each case these modelling exercises lead to structures which contain non-hexagonal rings. Finally, the use of fullerene-like models of microporous carbons to predict their adsorptive properties is summarised.

## **2. Graphitizing and non-graphitizing carbons**

In the early part of the 20th century it was established that carbons formed by the pyrolysis of organic materials fall into two distinct classes, cokes and chars. The two types of carbon have quite different physical properties. Cokes are relatively dense and soft whereas chars are hard, low density materials. Although cokes may be porous, this porosity is on a relatively large scale. Chars, on the other hand, have a high degree of microporosity, although some of this porosity is usually inaccessible to gases. The internal surface area can be enhanced by activation, i.e. mild oxidation with a gas such as carbon dioxide, steam or air. In this way surface areas of the order of  $2000 \text{ m}^2 \text{ g}^{-1}$  can be achieved. There is another key distinction between cokes and chars: the former can be converted into graphite by high temperature annealing while the

latter cannot. It is not entirely clear when this was first demonstrated, but it was certainly known in the 1940s. In a major review article published in 1948 [6], Paul Emmett describes work carried out by H.F. Johnston and G.L. Clark, who showed that “charcoals sinter and turn into graphite much less readily than does petroleum coke”. Unfortunately this work only seems to have been published in US government reports. The first detailed study of this topic to appear in the open literature is Rosalind Franklin’s classic 1951 paper [7]. Franklin prepared carbons from a wide range of organic materials, including sugar, polyvinylidene chloride (PVDC), polyvinyl chloride (PVC) and pitch. She then used X-ray diffraction to investigate the effect of heat treatment, up to a temperature of 3000 °C, on the structure of these carbons. She found that some of the carbons, including those prepared from PVC and pitch could be graphitized by heat treatments above about 2200 °C, while others, such as those prepared from sugar and PVDC, could not be transformed into crystalline graphite, even at 3000 °C. Instead, they formed a porous, isotropic material which only contained tiny domains of graphite-like structure. Franklin coined the terms “graphitizing” and “non-graphitizing” to describe these two classes of carbon.

### **3. Structure of non-graphitizing carbon: early work**

In his 1948 review Paul Emmett stated that “There are very few things about which we can be sure as regards the structure of charcoal.” However, he goes on to express the view that “The X-ray results taken as a whole constitute strong evidence that much of the carbon in charcoal is arranged in platelets”. Emmett’s idea seems to be that char consists of tiny flakes of graphene

1 approximately aligned with each other, giving a structure in which the pores  
2 have a slit-like shape. This picture of porosity in carbon as a system of  
3 interconnecting slits has proved extremely tenacious. In fact, it is still used in  
4 theoretical studies of adsorption and permeability of carbons [e.g. 8,9].  
5  
6 However, there is little experimental evidence that the pores in non-  
7 graphitizing carbon are generally slit-like in shape. Franklin's 1951 X-ray  
8 diffraction study demonstrated rather the opposite, as can be seen from Fig.  
9 1, which shows her models for non-graphitizing and graphitizing carbons. In  
10 these models, the basic units are small graphitic crystallites containing a few  
11 layer planes, which are joined together by cross-links. For the non-graphitizing  
12 carbon (Fig. 1(a)), the structural units are oriented randomly, so that the  
13 structure is isotropic, while in the graphitizing carbon (Fig. 1(b)) the units are  
14 approximately parallel to each other. It is clear that the structure in Fig. 1(b) is  
15 more amenable to transformation into graphite.

16  
17 Franklin's ideas on graphitizing and non-graphitizing carbons are probably  
18 broadly correct, but they are in some regards incomplete. For example, the  
19 nature of the cross-links between the graphitic fragments is not specified, so the  
20 reasons for the sharply differing properties of graphitizing and non-graphitizing  
21 carbons is not explained. Some authors have suggested that the "cross-links"  
22 envisaged by Franklin might in fact be  $sp^3$ -bonded atoms [e.g. 10]. The  
23 presence of diamond-like domains would be consistent with the hardness of  
24 non-graphitizing carbons, and might also explain their extreme resistance to  
25 graphitization. A problem with these models is that  $sp^3$  carbon is unstable at  
26 high temperatures: diamond is converted to graphite at 1700°C. Therefore, the



1 presence of  $sp^3$  atoms in a carbon is unlikely to explain the resistance of the  
2 carbon to graphitization at high temperatures, although the presence of small  
3 amounts of  $sp^3$  carbons cannot be ruled out. It should also be noted that  
4 diffraction studies of non-graphitizing carbons have found no evidence for the  
5 presence of  $sp^3$ -bonded atoms [11].  
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14 Transmission electron microscopy began to play a major role in the structural  
15 study of carbon in the 1970s, when improvements in lens design meant that  
16 the interlayer (0.34 nm) graphitic spacing could be readily resolved [12]. In  
17 1975, Ban, Crawford and Marsh described a lattice-resolution TEM study of  
18 non-graphitizing carbons derived from polyvinylidene chloride [13]. The  
19 structures of the carbons following heat treatments at temperatures in the range  
20 530 °C - 2700 °C was investigated. Images of these carbons apparently showed  
21 the presence of curved graphite sheets, typically two or three layer planes thick,  
22 enclosing voids. These images led Ban *et al.* to suggest that heat treated non-  
23 graphitizing carbons have a ribbon-like structure. A rather similar model for the  
24 structure of glassy carbon had been proposed by Jenkins and Kawamura in  
25 1971 [14]. However, models of this kind have serious weaknesses. Such models  
26 consist of curved and twisted graphene sheets enclosing irregularly-shaped  
27 pores. However, graphene sheets are known to be highly flexible, and would  
28 therefore be expected to become ever more closely folded together at high  
29 temperatures, in order to reduce surface energy. Indeed, tightly folded graphene  
30 sheets are quite frequently seen in carbons which have been exposed to  
31 extreme conditions. Thus, structures like the ones envisaged by Jenkins, Ban  
32 and their colleagues would be unlikely to be stable at very high temperatures. It  
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has also been pointed out by Oberlin [15] that the ribbon-like models are based on a questionable interpretation of the electron micrographs. In most micrographs of graphitized carbons, only the {002} fringes are resolved, and these are only visible when they are approximately parallel to the electron beam. Therefore, such images tend to have a ribbon-like appearance. However, since only a part of the structure is being imaged, this appearance can be misleading, and the true three-dimensional structure may be more cage-like than ribbon-like.

#### **4. Structure of non-graphitizing carbon: fullerene-related models**

The discovery of the fullerenes [16 - 18] and subsequently of related structures such as carbon nanotubes [19,20] and nanohorns [21,22], has given us a new paradigm for 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 new perspective prompted a number of groups to 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 to consider the idea that non-graphitizing, microporous carbon might have a structure related to that of the fullerenes were published in 1997 [4,5]. A series of subsequent papers developed the idea further [23 - 26]. In the original studies, some non-graphitizing carbons were examined using transmission electron microscopy 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

1 and graphitizing carbons prepared at 1000 °C are shown in Fig. 2. The insets  
2 show diffraction patterns recorded from areas approximately 0.25 μm in  
3 diameter. The image of the non-graphitizing carbon shows the structure to be  
4 disordered and isotropic, consisting of tightly curled single carbon layers, with no  
5 obvious graphitization. The diffraction pattern shows symmetrical rings,  
6 confirming the isotropic structure. The appearance of graphitizing carbon, on the  
7 other hand, approximates much more closely to that of graphite. In this case the  
8 structure contains small, approximately flat carbon layers, packed tightly  
9 together with a high degree of alignment. The fragments can be considered as  
10 rather imperfect graphene sheets. The diffraction pattern for the graphitizing  
11 carbon consists of arcs rather than symmetrical rings, confirming that the layers  
12 are preferentially aligned along a particular direction. The bright, narrow arcs in  
13 this pattern correspond to the interlayer {002} spacings, while the other  
14 reflections appear as broader, less intense arcs.

35  
36 Micrographs showing the effect of high temperature heat treatments on the  
37 structure of non-graphitizing and graphitizing carbons are shown in Fig. 3 (note  
38 that the magnification here is much lower than for Fig. 2). In the case of the non-  
39 graphitizing carbon, heating at 2300 °C in an inert atmosphere produces the  
40 disordered, porous material shown in Fig. 3 (a). This structure is made up of  
41 curved and faceted graphitic layer planes, typically 1 - 2 nm thick and 5 – 15 nm  
42 in length, enclosing randomly-shaped pores. A few somewhat larger graphite  
43 crystallites are present, but there is no macroscopic graphitization. In contrast,  
44 heat treatment of the anthracene-derived carbon produces large crystals of  
45 highly ordered graphite, as shown in Fig. 3 (b).

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2 More detailed analysis of the heat-treated non-graphitizing carbons showed that  
3  
4 they often contained closed nanoparticles; examples can be seen in Fig. 4. The  
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6 particles were usually faceted, and often hexagonal or pentagonal in shape.  
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8 Sometimes, faceted layer planes enclosed two or more of the nanoparticles, as  
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10 shown in Fig. 4 (b). Here, the arrows indicate two saddle-points, which are  
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12 indicative of heptagonal rings, as pointed out by Iijima and colleagues [27]. The  
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14 closed nature of the nanoparticles, their hexagonal or pentagonal shapes, and  
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16 other features such as the saddle-points strongly suggest that the particles have  
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18 fullerene-like structures. Indeed, in many cases the particles resemble those  
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20 produced by arc-evaporation in a fullerene generator although in the latter case  
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22 the particles usually contain many more layers.  
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31 The observation of fullerene-related nanoparticles in the heat treated carbons  
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33 suggested that the original, freshly-prepared carbons may also have had  
34  
35 fullerene-related structures. This prompted the present author and colleagues to  
36  
37 propose a model for the structure of non-graphitizing carbons which consists of  
38  
39 discrete fragments of curved carbon sheets, in which pentagons and heptagons  
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41 are dispersed randomly throughout networks of hexagons, as shown in Fig. 5. It  
42  
43 should be noted that this representation of the structure is intended as an  
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45 illustration, rather than a full, three-dimensional model. In subsequent work,  
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47 discussed in section 7, three-dimensional structures have been created from the  
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49 curved fragments, and have been used to model adsorption.  
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## 5. Experimental evidence for fullerene-related structure of non-graphitizing carbon

The micrographs shown in Figs. 2, 3 and 4 were recorded using conventional transmission electron microscopy. The resolution achievable with such microscopes is typically around 0.18 nm. In the past 10 years or so, a new generation of TEMs has become available with resolutions of 0.05 nm or better. This has been achieved through the use of aberration-correctors, which compensate for the inherent defects of electron lenses [28]. These microscopes are capable of resolving carbon atoms in graphene, where the atomic spacing is 0.142 nm [29, 30]. In 2008, Suenaga, Liu and the present author applied this technique for the first time to a microporous carbon [31]. The carbon studied was a commercial activated carbon, Norit GSX. Imaging was carried out in an aberration-corrected TEM operated at 120kV, with a point resolution of better than 0.14 nm. Obtaining atomic resolution images of the fresh carbon proved to be extremely challenging, and the images which were recorded were difficult to interpret. A typical example is shown in Fig. 6. At the edge of this fragment the individual rings of carbon atoms are resolved: the bright spots represent the centres of the rings. In some cases, pentagonal arrangements of spots can be discerned: an example is arrowed. However, the images of the fresh carbon were not of sufficient quality to provide definite proof of the presence of pentagons.

Much better quality images could be obtained from carbon samples which had been heated at high temperature, in order to increase the crystallinity. An image from a carbon sample which had been heated in Ar to 2000 °C is shown

1 in Fig. 7 (a). Here there is clear evidence for the presence of five-membered  
2 rings. The area enlarged in Fig. 7 (b) shows an arrangement of 5 bright spots  
3 surrounding a central spot. A good match was obtained with the simulated  
4 image in Fig. 7 (c), which was obtained from the structure in Fig. 7 (d) using a  
5 standard multi-slice procedure. Here, the pentagon is oriented approximately  
6 parallel to the plane of the image. A second area which contains a pentagonal  
7 structure is shown in Fig. 7 (e). In this case the central pentagonal ring is not  
8 visible, apparently because the ring is tilted away from the plane of the image.  
9 Support for this comes from the reasonable match which can be seen  
10 between the image and the simulated image in Fig. 7 (f), obtained from the  
11 structure in Fig. 7 (g). Images of this kind provide convincing evidence for the  
12 presence of pentagonal carbon rings in the heat-treated carbon.  
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31 In addition to high resolution imaging, TEM can also probe the structure of  
32 material through the use of electron energy loss spectroscopy (EELS). In 2011,  
33 Zhang *et al.* used EELS to investigate the structure of a non-graphitizing  
34 carbon derived from phenolic resin [32]. In this study a detailed analysis was  
35 carried out of the carbon K-edge spectrum. When the C=C  $\pi^*$ , C—C  $\sigma^*$  and  
36 C=C  $\sigma^*$  components were removed from the spectrum, a residual feature was  
37 found between 286 and 288 eV. A similar feature is observed in spectra  
38 recorded from crystalline C<sub>60</sub> [33] and could therefore be interpreted as  
39 evidence for five-membered rings. As Zhang *et al.* point out, further theoretical  
40 modelling would be valuable in confirming this interpretation.  
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Evidence for fullerene-like structures in microporous carbons has also been found using Raman spectroscopy. Burian, Dore and colleagues have used this method to analyse carbons prepared from sucrose, heat treated at temperatures from 1000 °C - 2300 °C [34, 35]. The Raman spectra showed clear evidence for the presence of fullerene- and nanotube-like elements in the carbons.

X-ray and neutron diffraction studies have generally been less useful than microscopy and spectroscopy in establishing whether microporous carbons have a fullerene-related structure, since the interpretation of diffraction data from these highly disordered materials is not straightforward. Burian, Dore and their co-workers have published a number of studies in this area [e.g. 36, 37] and have found that the results are consistent with the presence of non-six membered rings, but other interpretations may also be possible.

## **6. Modelling the structural evolution of microporous carbon**

The formation mechanism of microporous carbon is not well understood at the atomic level. A number of groups have attempted to model the process, and in several cases these modelling exercises have produced structures which contain fullerene-like elements. One of the first such exercises was reported by Acharya *et al.* in 1999 [38]. In this work the carbon was assumed to be derived from polyfurfuryl alcohol. The starting point for the simulation was a series of all-hexagon fragments, terminated with hydrogens, as shown in Fig. 8 (a), while Figs. 8 (b) – (d) illustrate the evolution of the structure as the H/C ratio is reduced (i.e. the temperature is increased). During this evolution,

1 pentagons and heptagons form as well as hexagons, resulting in the formation  
2 of curved fragments.  
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7 In a later study, Kumar *et al.* used Monte Carlo (MC) simulations to model the  
8 evolution of a polymer structure into microporous carbon [39]. Again  
9 polyfurfuryl alcohol was chosen as the precursor, and in this case the starting  
10 structure was the polymer itself rather than hexagonal fragments of carbon.  
11 Simulations were carried out with a number of different polymer starting  
12 structures and different pre-defined densities. In each case the final carbon  
13 was made up of a hexagonal network with 10-15 % non-hexagonal rings  
14 (pentagons and heptagons). The properties of the simulated carbons  
15 appeared to be generally consistent with experimental results.  
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31 A different approach to modelling the evolution of microporous carbon was  
32 used by Shi [40]. Here, the initial system consisted of carbon gas atoms at  
33 very high temperature. This choice of initial condition was intended to  
34 represent the high temperature state in a pyrolysis process after the polymer  
35 chains break down and most other elements have evaporated. The  
36 temperature was then decreased so that the atoms “condensed” to form a  
37 porous structure composed of curved and defected graphene sheets, in which  
38 the curvature was induced by non-hexagonal rings.  
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53 In 2009, Powles, Marks and Lau described a comprehensive molecular-  
54 dynamics study of the self-assembly of carbon nanostructures [41]. The  
55 precursor for these simulations was highly disordered amorphous carbon, which  
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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 the highly curved  $sp^2$  sheet structure shown in Fig. 9. The resemblance between this and the structure shown in Fig. 5 is very striking.

## **7. Modelling adsorption using fullerene-like models for microporous carbon**

To date, there have been relatively few attempts to use fullerene-like models to predict the adsorptive and other properties of microporous carbons. By far the most ambitious programme of work in this area has been carried out by Terzyk, Gauden and colleagues, whose results have been published in a series of papers beginning in 2007 [42 - 49]. In the first of these [42], 36 different carbon structures with increasing microporosity, labelled S0 - S35, were generated. The initial microporous structure, named S0, is shown in Fig. 10 (top left). Fragments were then progressively added to create the 36 structures labelled S0 - S35. Pore size distribution (PSD) curves for the structures were calculated using the method of Bhattacharya and Gubbins (BG) [50]. This involves determining the statistical distribution of the radii of the largest sphere that can be fitted inside a pore at a given point. A selection of the PSD curves determined in this way is shown in Fig. 11. It can be seen that the most "crowded" structure, S35, has a much narrower range of pore sizes than the initial S0 structure. Argon adsorption isotherms were simulated for these structures using the parallel tempering Monte Carlo simulation method developed by Yan and de Pablo [51]. Some of these isotherms are

1 shown in Fig. 12. These show that the gradual crowding of the S0 structure  
2 (leading finally to S35) leads to a decrease in the maximum number of  
3 adsorbed molecules. On the other hand, the S0 structure exhibits less  
4 adsorption at low pressures than the more crowded ones because the  
5 average micropore diameter is larger. Also notable is the increasing  
6  
7 “sharpness” of the inflection point in the isotherms, a feature which is often  
8 reported for experimental systems (e.g. [52]). The simulated isotherms were  
9 then used to determine PSD curves, using a range of widely used methods,  
10 with the aim of checking the validity of these methods. Good agreement was  
11 found between the PSDs determined from the isotherms and the PSDs from  
12 the BG method. This confirms the validity of various methods for calculating  
13 PSD curves from adsorption data. It would also seem to confirm the validity of  
14 the fullerene-related model for microporous carbon.  
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17 In the next paper of this series [43], Terzyk *et al.* began with 3 structures  
18 constructed from fullerene-like fragments, as shown in Fig. 13. The densities  
19 of these structures were calculated, and values in the range 2.18 - 2.24 g cm<sup>-3</sup>  
20 were found, consistent with typical densities of non-graphitizing carbons.  
21 Once again, pore size distributions for the structures were determined using  
22 the BG method. As in the previous paper, the simulated isotherms were used  
23 to determine PSD curves, using a range of widely used methods. Good  
24 agreement was found between the PSDs determined from the simulated  
25 adsorption data and the original PSDs from the BG method. This is illustrated  
26 in Fig. 14, where the PSD curve determined from the Bhattacharya-Gubbins  
27 method is compared with results from the Horvath–Kawazoe method [53].  
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2 In a further paper [44], the adsorption of Ne, Ar, Kr, Xe, CCl<sub>4</sub> and C<sub>6</sub>H<sub>6</sub> on the  
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4 S0 and S35 carbons was modelled. The simulated data were compared with  
5  
6 the predictions of the Dubinin–Radushkevich [54] and Dubinin–Astakhov [55]  
7  
8 adsorption isotherm equations, and a good fit was found for the S35 carbon.  
9  
10 For the S0 carbon the Dubinin–Izotova (DI) equation [56] gave a better fit  
11  
12 because the micropores in this model have a wide distribution of diameters.  
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14 The simulated isotherms exhibited a number of features similar to those seen  
15  
16 in experimental results. For example the isotherms for CCl<sub>4</sub> and C<sub>6</sub>H<sub>6</sub> were  
17  
18 temperature invariant, as observed experimentally. It was also noted that the  
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20 isotherms obeyed Gurvich’s rule, which states that the larger the molecular  
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22 collision diameter the smaller the access to micropores, as well as other  
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24 empirical and fundamental correlations developed for adsorption on  
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26 microporous carbons.  
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36 The effect of oxidising the carbon surface on porosity was analysed in a paper  
37  
38 published in 2009 [45]. A “virtual oxidation” procedure was employed, in which  
39  
40 surface carbonyls were attached to carbon atoms located on the edges of the  
41  
42 fragments. It was assumed that the structure of the carbon skeleton remained  
43  
44 unchanged. Pore size distributions, determined using the BG method were  
45  
46 found not to be greatly affected by oxidation. Simulated isotherms for Ar, N<sub>2</sub>  
47  
48 and CO<sub>2</sub> were calculated using the GCMC method. For Ar, the effect of  
49  
50 oxidation on the isotherm was relatively small. However, for N<sub>2</sub> and CO<sub>2</sub> there  
51  
52 were significant changes in the isotherms, due to electrostatic interactions  
53  
54 between N<sub>2</sub> and CO<sub>2</sub> and the surface carbonyl groups. As a consequence of  
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1 this, pore size distributions calculated from the simulated isotherms for N<sub>2</sub> and  
2 CO<sub>2</sub> differed markedly from those originally determined from the BG method.  
3  
4 An important conclusion from this is that experimental PSDs determined using  
5 CO<sub>2</sub> (or using N<sub>2</sub> if there is a large oxygen content) may be unreliable. A  
6  
7 further study looked at the influence of carbon surface oxygen groups on  
8  
9 Dubinin-Astakhov equation parameters calculated from CO<sub>2</sub> isotherms [46]. It  
10  
11 was concluded that porosity parameters calculated by fitting the DA model to  
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13 experimental CO<sub>2</sub> adsorption data may be questionable.  
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22 Terzyk and colleagues have published a number of other studies in which  
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24 fullerene-like models have been used to predict the properties of microporous  
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26 carbons [47 - 49], but the results summarised above are sufficient to  
27  
28 demonstrate the utility of such models.  
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## 36 **8. Discussion**

37 The structure of microporous carbon has been a subject of uncertainty for  
38  
39 decades, and a wide range of different structural models have been proposed.  
40  
41 The idea discussed in this review, that microporous carbon has a structure  
42  
43 related to that of the fullerenes, is by no means universally accepted, and will  
44  
45 remain controversial until unequivocal experimental evidence is obtained. The  
46  
47 best hope of achieving such proof probably lies with aberration-corrected  
48  
49 transmission electron microscopy. As discussed in Section 5, the advent of this  
50  
51 new form of TEM has meant that directly imaging the ring structure of graphitic  
52  
53 carbons is now a practical possibility. Initial studies using this technique [31]  
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1 have produced convincing evidence for pentagonal rings in carbon heated to  
2 2000 °C, but further work is needed to achieve clear images of pentagons in  
3  
4 “fresh” carbon. This is clearly a considerable experimental challenge, but not  
5  
6 beyond the capabilities of current microscopes.  
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10  
11 While direct imaging probably provides the best hope of finally determining the  
12 structure of microporous carbon, other techniques can give valuable  
13 corroborative information. We have seen that careful analysis of electron energy  
14 loss spectra has revealed features that can be ascribed to five-membered rings  
15 [32]. More work in this area, involving both experimental studies and  
16 theoretical analysis would be welcome, as would further studies using  
17 techniques such as Raman spectroscopy and X-ray and neutron diffraction.  
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31 If experimental evidence for a fullerene-related structure appears to be growing,  
32 theoretical studies of the formation of microporous carbon also point in the  
33 same direction. It is surely significant that four separate modelling studies, all  
34 using slightly different methods and starting systems [38 - 41], each produce  
35 structures containing non-hexagonal rings. Particularly notable is the  
36 resemblance between the structure of Powles and colleagues (Fig. 9), and the  
37 structure inferred from TEM observations shown in Fig. 5. There is clearly  
38 scope for further modelling work on the evolution of carbonaceous material  
39 into carbon, since there is still much that we do not understand. In particular,  
40 the question of why some materials yield non-graphitizing carbon while others  
41 give graphitizing carbon is not at all well understood at the molecular level.  
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A fullerene-like model for microporous carbon could be of great value in understanding its adsorptive properties. It is widely recognised that the slit pore model has serious deficiencies [57 - 61], and it has been known for some time that the profile for small-angle (X-ray or neutron) scattering does not correspond to the model predictions for slit scattering. However, a widely-accepted alternative model has not yet emerged. Theoretical studies by Terzyk *et al.* [42 - 49] have shown that fullerene-like models can replicate reasonably well the densities, pore size distributions and adsorption isotherms observed experimentally, and it would be valuable if other groups were to carry out similar studies. One way in which the modelling work could be extended would be by employing larger fragments. It is very difficult to determine accurately the size of the individual fragments in microporous carbon, but recent work by Kyotani and colleagues has suggested that they may be larger than generally thought [62]. In this work, the amount of hydrogen in carbon materials heat-treated to 1000°C and above was measured. The crystallite sizes were then determined by assuming that all the edge sites were terminated by hydrogen atoms. In this way it was found that a non-graphitizing carbon prepared from polyfurfuryl alcohol by heating to 1000°C had a crystallite size of 12 nm, much larger than the size estimated from X-ray diffraction (1 nm). This is understandable, since XRD measurements assume planar crystallites, and the structures in a non-graphitizing carbon are of course highly curved. A graphene crystallite with a diameter of 12 nm would contain approximately 4500 atoms, whereas the fragments employed by Terzyk *et al.* generally had fewer than 500 atoms. It is quite possible that structures constructed from larger fragments would

display similar behaviour to those made from smaller ones, but further modelling studies are needed to confirm this.

## Acknowledgements

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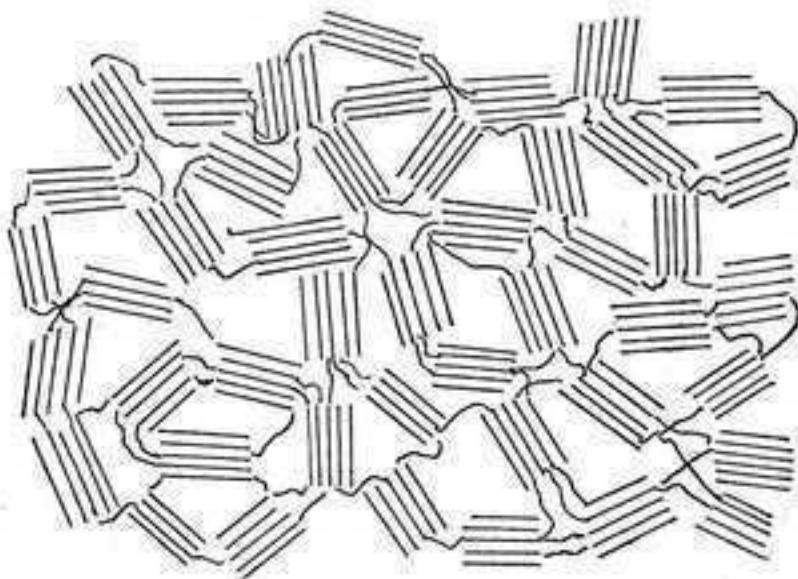
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## 40 Figure Captions

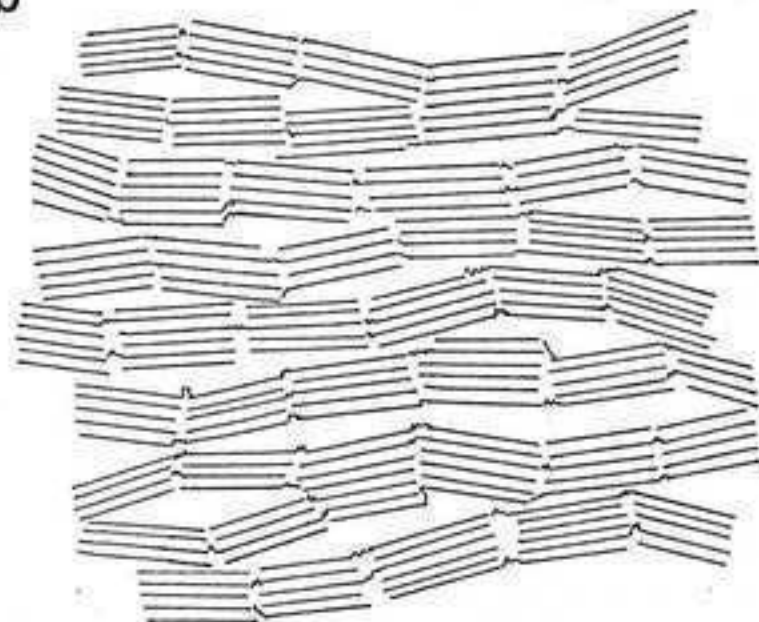
- 41  
42  
43 Figure 1 Franklin's representations of (a) non-graphitizing and (b)  
44 graphitizing carbons [7].  
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47 Figure 2 (a) High resolution TEM image of carbon prepared by pyrolysis  
48 of sucrose in nitrogen at 1000 °C, (b) carbon prepared by  
49 pyrolysis of anthracene at 1000 °C. Insets show selected area  
50 diffraction patterns [23].  
51  
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53 Figure 3 Micrographs of (a) sucrose carbon and (b) anthracene carbon  
54 following heat treatment at 2300 °C [24].  
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57 Figure 4 (a) Micrograph showing closed structure in PVDC-derived  
58 carbon heated at 2600 °C, (b) another micrograph of same  
59 sample, with arrows showing regions of negative curvature [4].  
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- Figure 5 Schematic illustration of a model for the structure of non-graphitizing carbons based on fullerene-like elements.
- Figure 6 Aberration-corrected HRTEM micrograph of fresh activated carbon, with arrow indicating possible pentagonal arrangement of carbon rings [31].
- Figure 7 (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) [31].
- Figure 8 Structural evolution of microporous carbon modelled by Acharya *et al.* [38]. The sequence of images (a) to (d) represent decreasing H/C ratio (or equivalently, increasing temperature).
- Figure 9 Curved  $sp^2$  sheet structure produced in molecular-dynamics simulations by Powles *et al.* [41].
- Figure 10 Illustration of the construction of microporous structures S0, S16 and S35 from fullerene-related fragments. These structures are used by Terzyk *et al.* to simulate adsorption properties [42].
- Figure 11 Pore size distribution curves for some of the model structures created by Terzyk *et al.* [42].
- Figure 12 Argon adsorption isotherms for model structures [42].
- Figure 13 Illustration of the construction of micro-mesoporous structures, from the work of Terzyk *et al.* [43]. (i) shows individual fullerene-related fragments, (ii) shows a 2D structure constructed from these fragments. H0 is the initial 3D structure produced from the fragments; HC1 and HC2 were created by cutting boxes from this structure.
- Figure 14 Comparison of pore size distribution curves for the H0 structure determined using the Bhattacharya-Gubbins and the Horvath–Kawazoe method [43].

**a**



**b**



**Fig. 1**

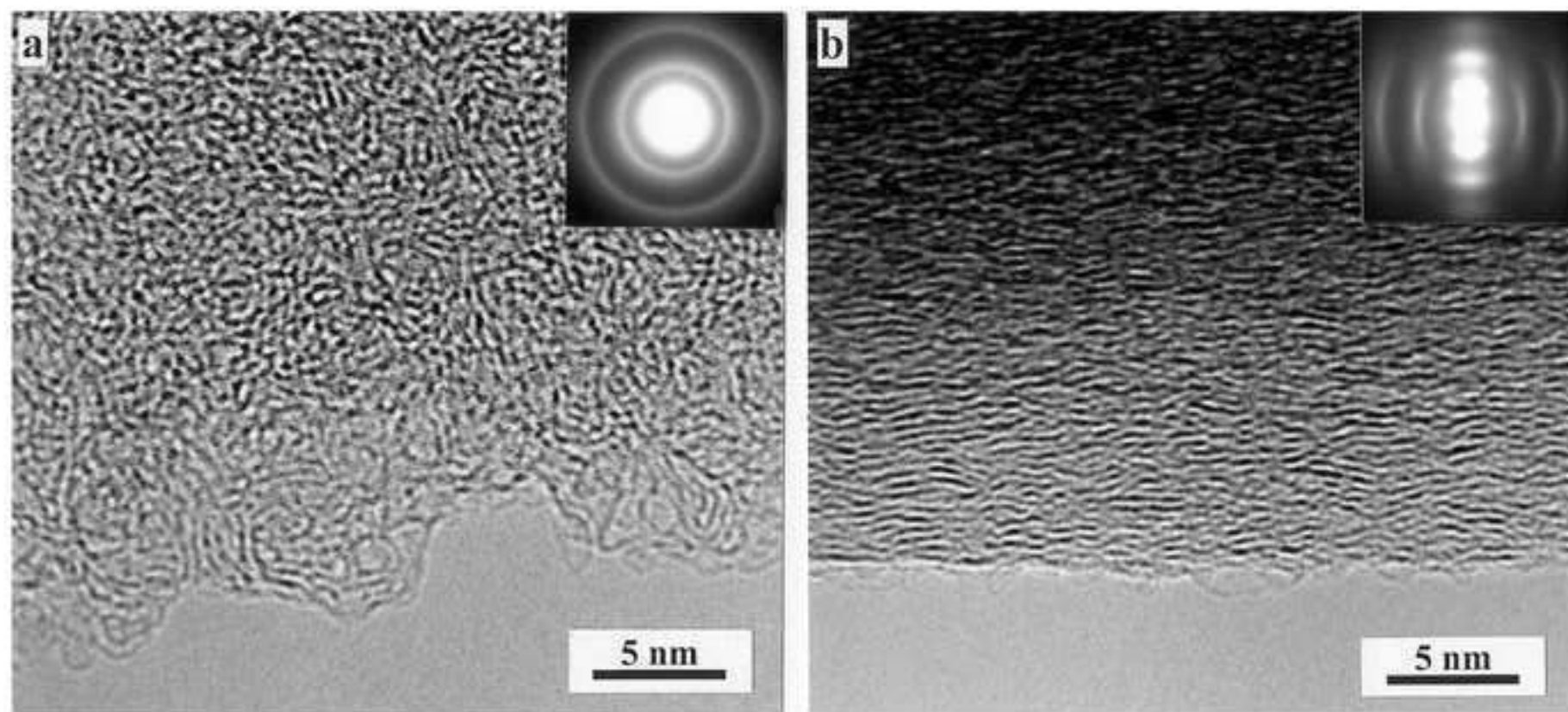


Fig. 2

Figure 3  
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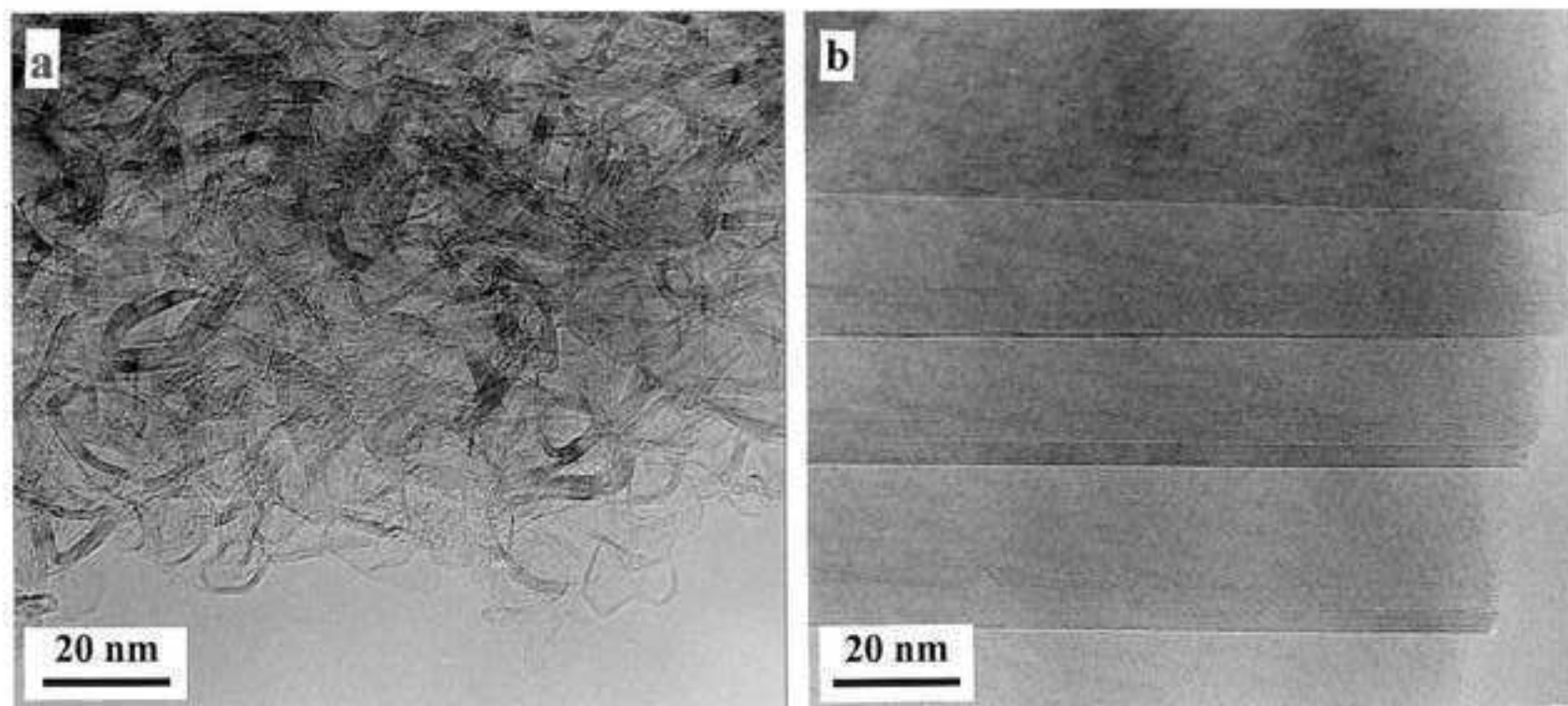


Fig. 3



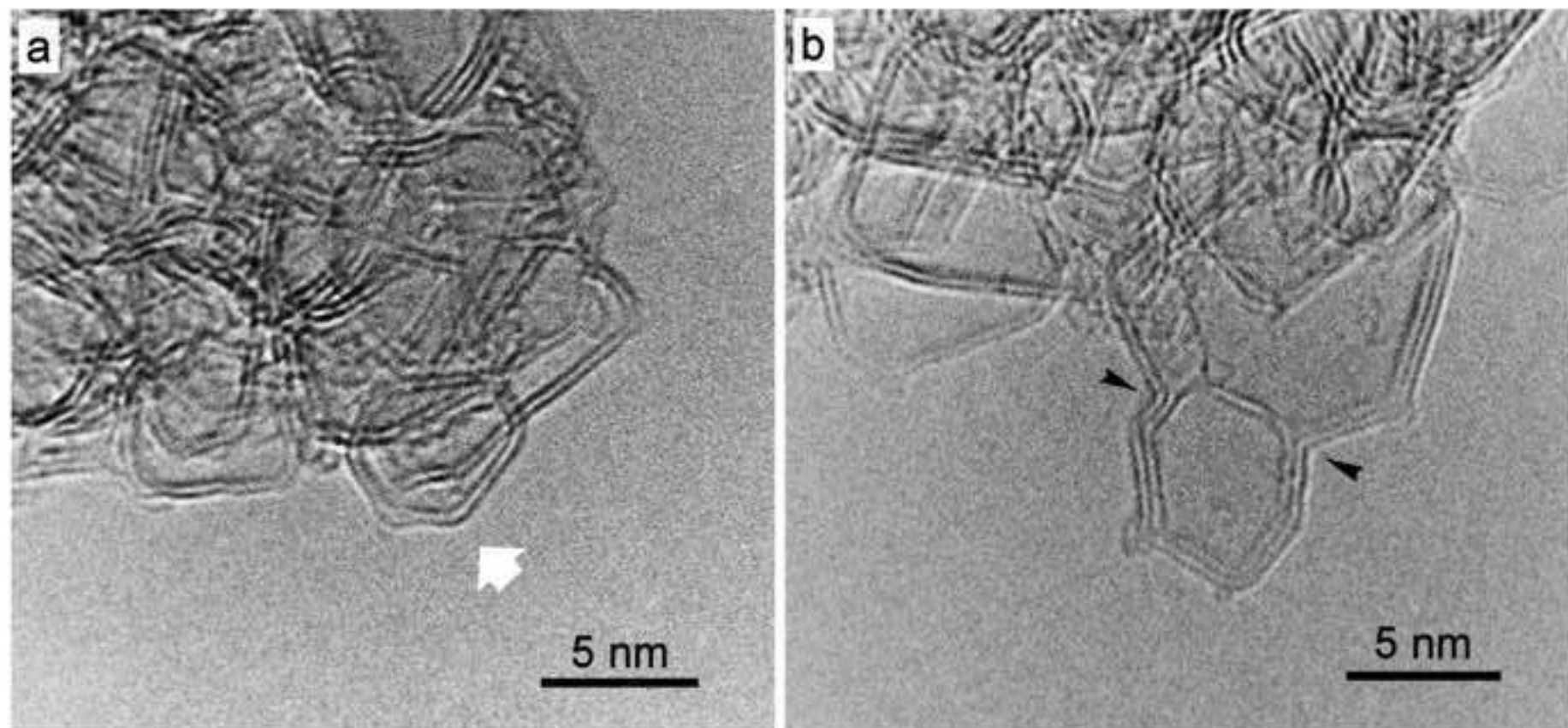
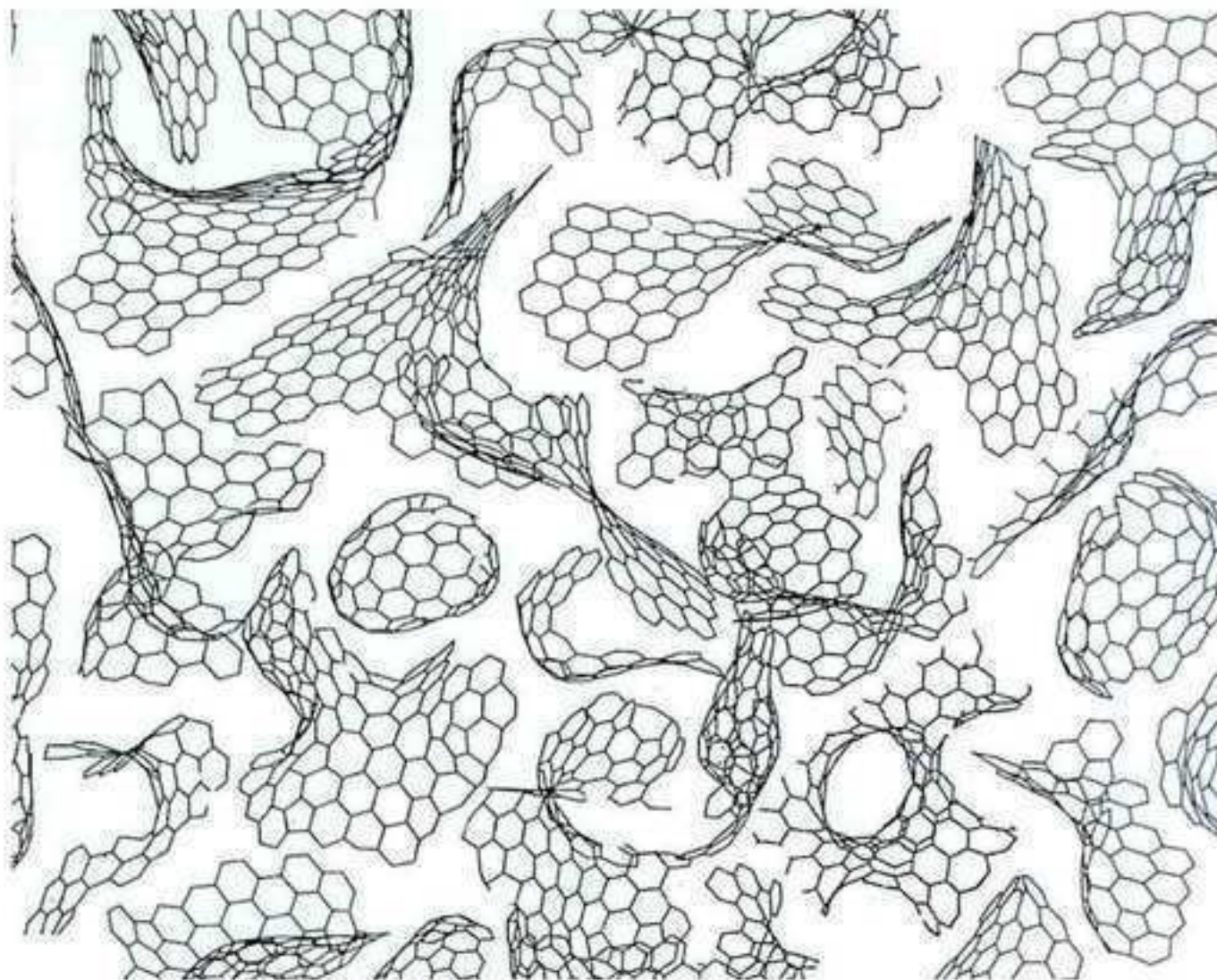


Fig. 4

Figure 5  
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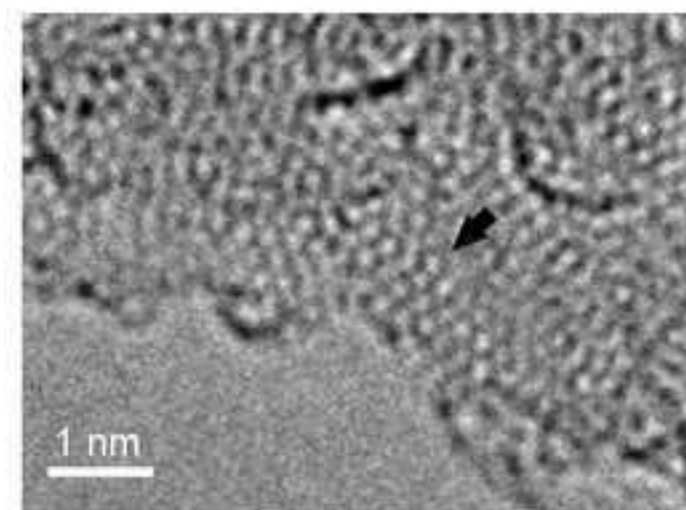


**Fig. 5**



Figure 6

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**Fig. 6**

Figure 7  
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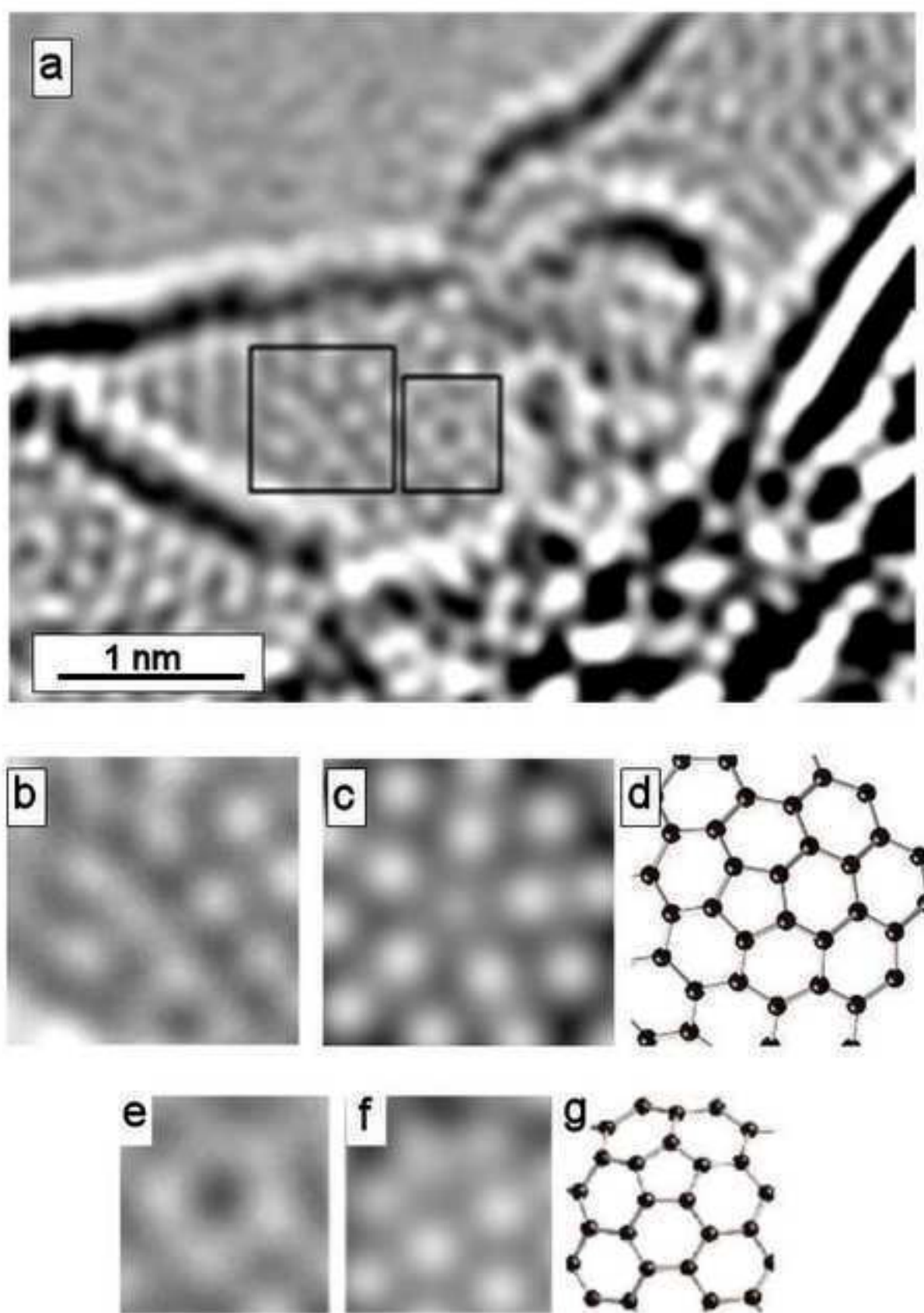
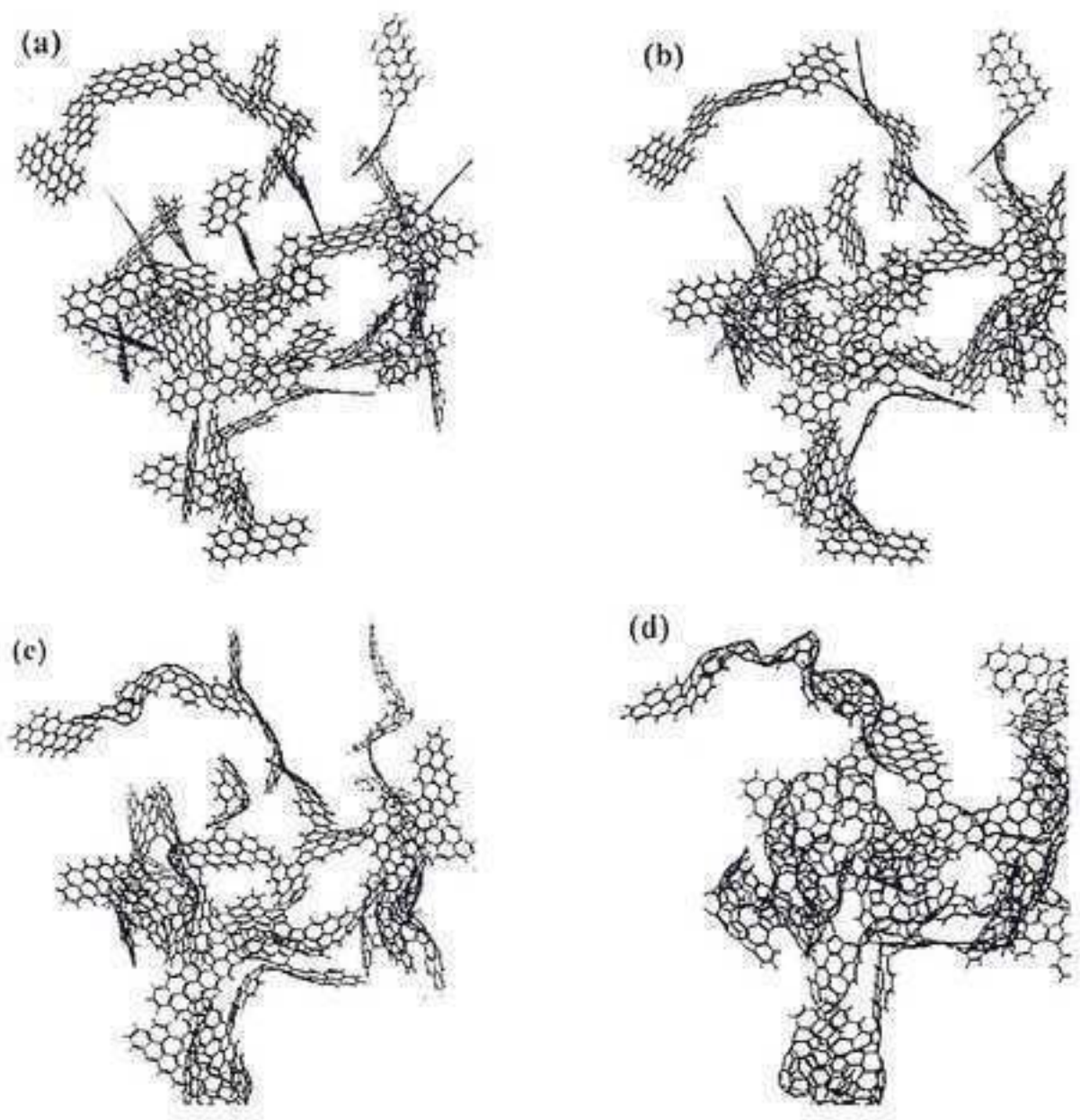
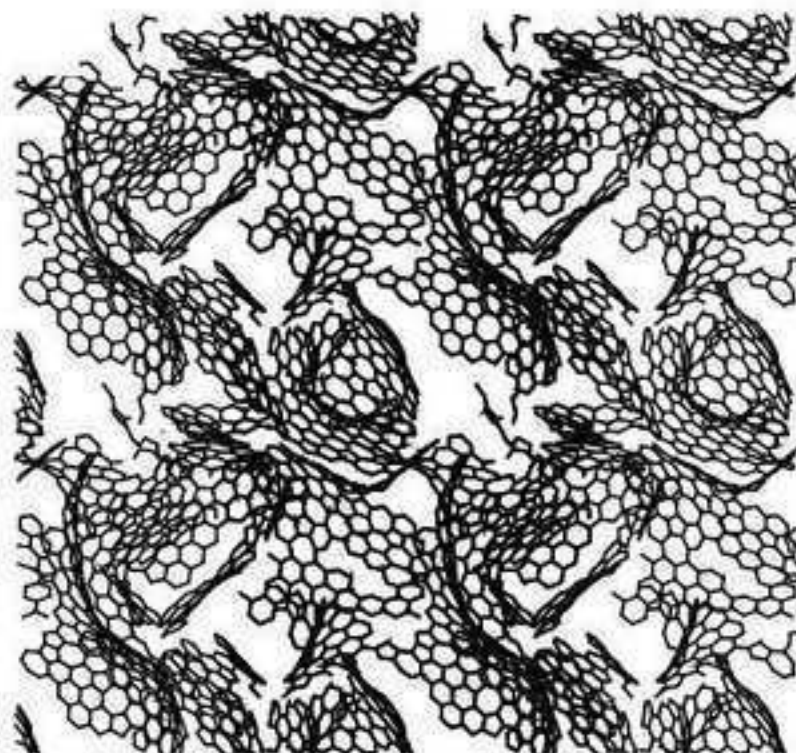


Fig. 7

Figure 8  
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**Fig. 9**

Figure 10  
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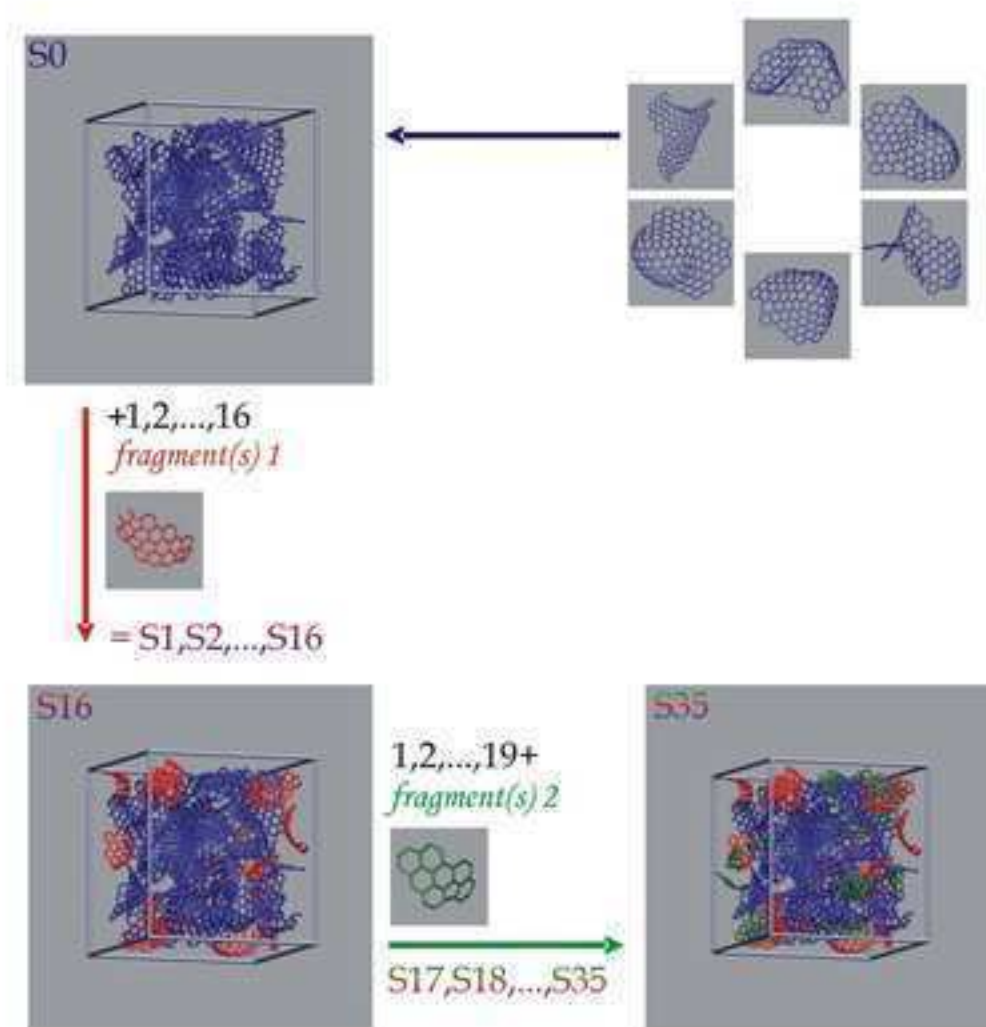


Fig. 10



Figure 11  
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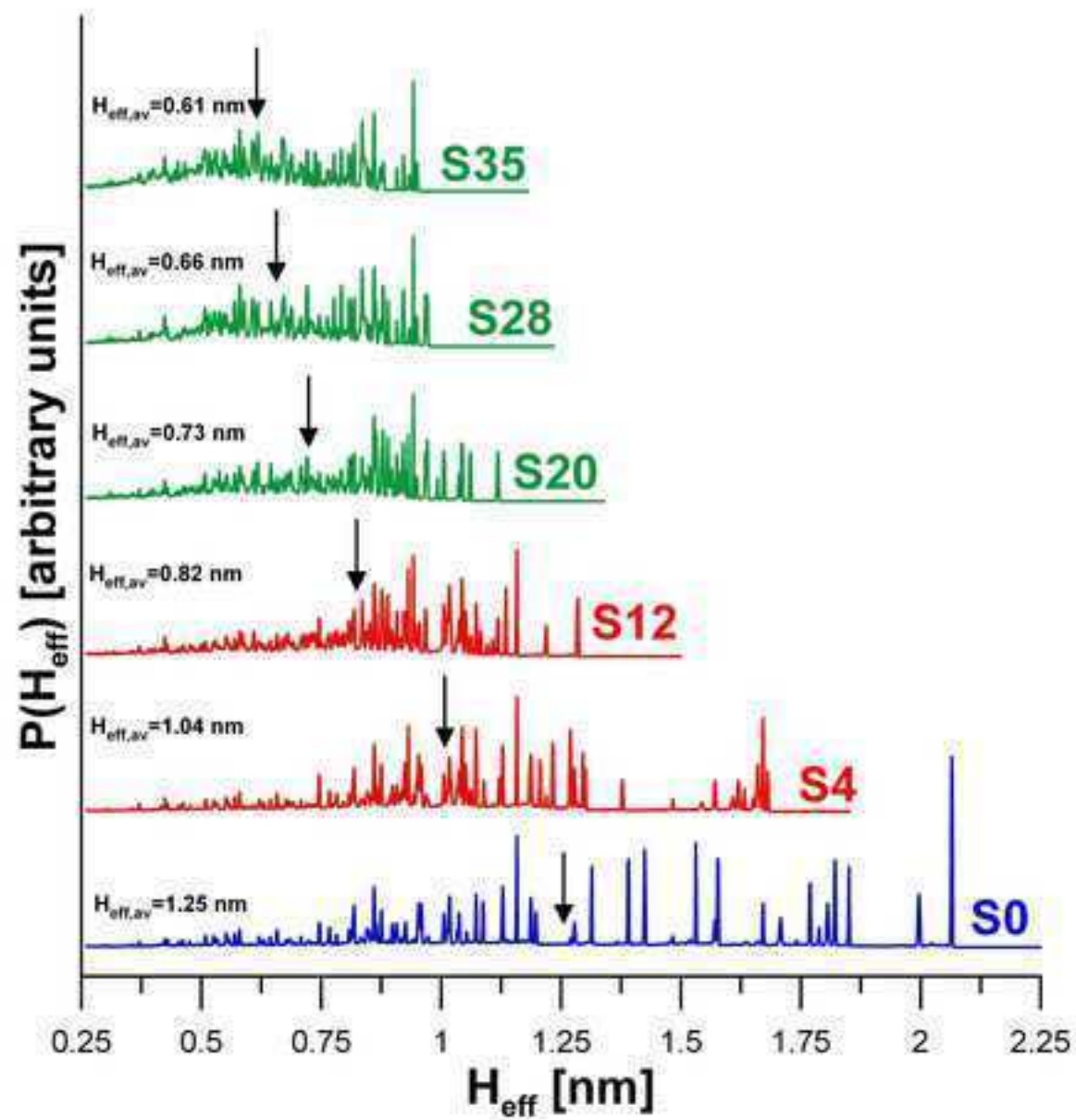


Fig. 11

Figure 12  
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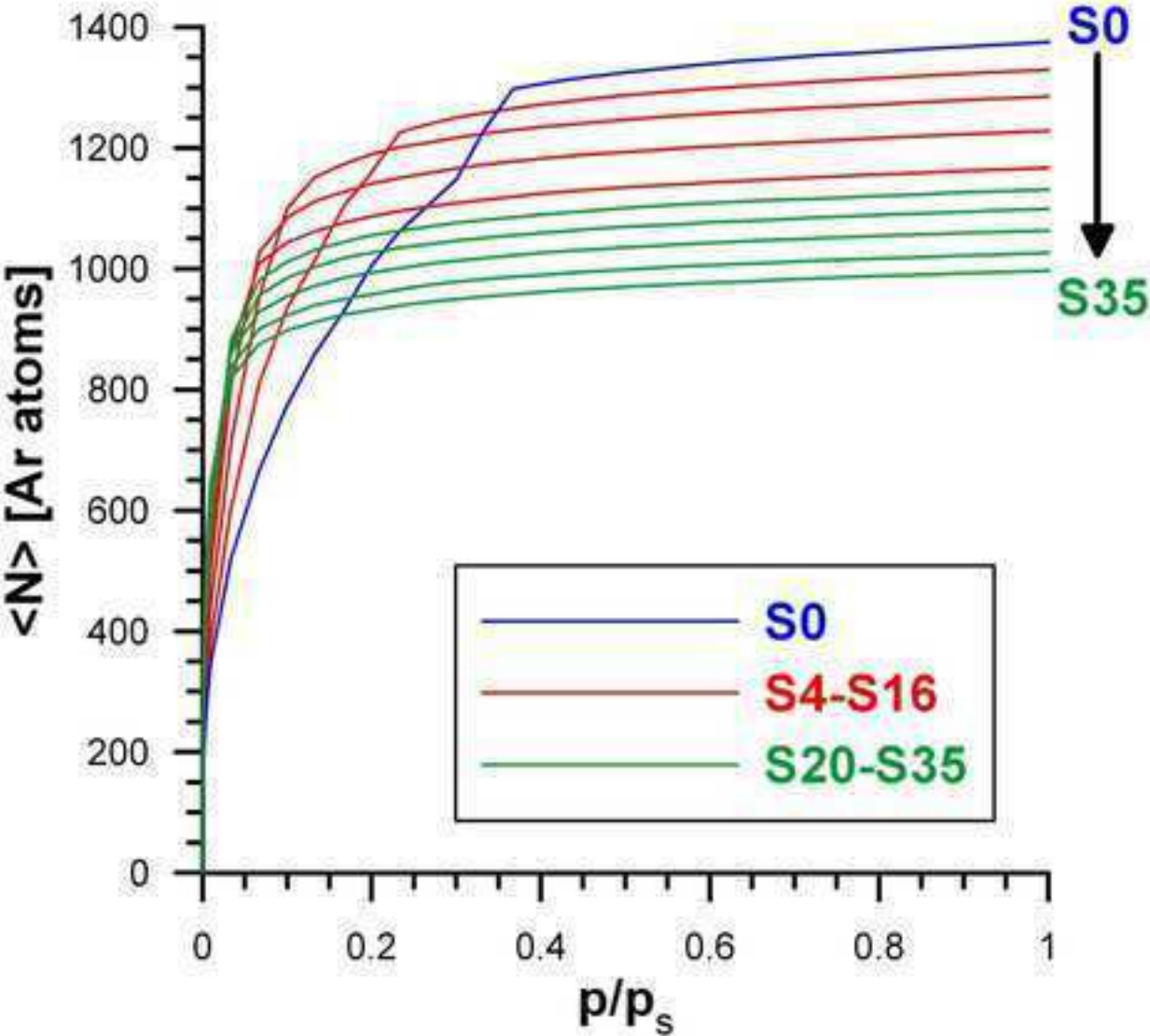


Fig. 12

Figure 13  
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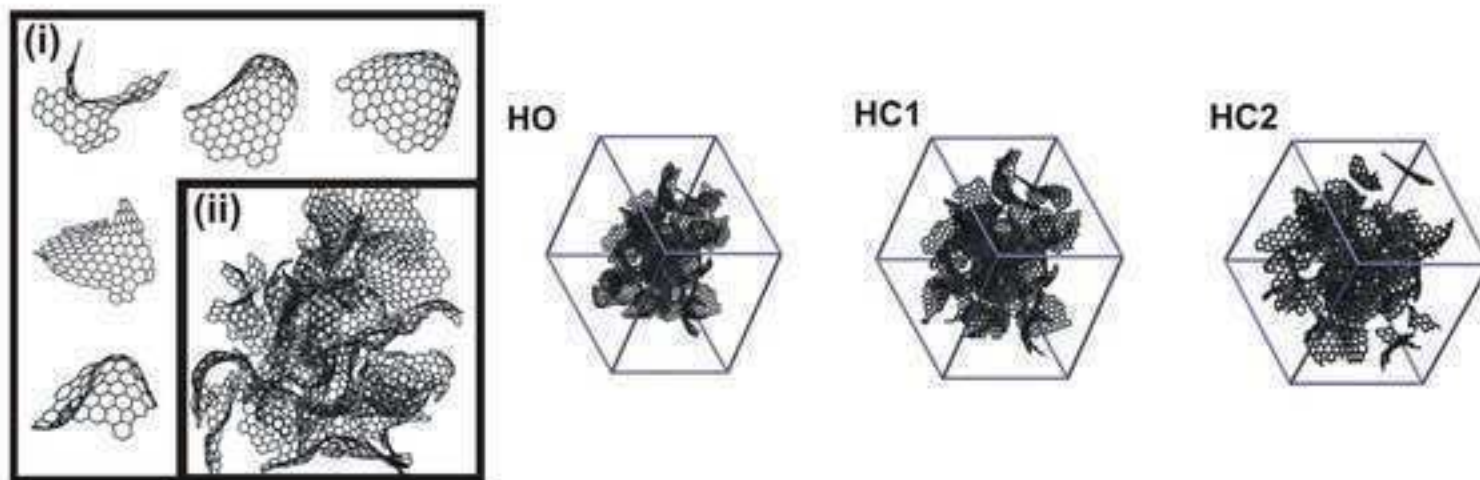


Fig. 13



Figure 14  
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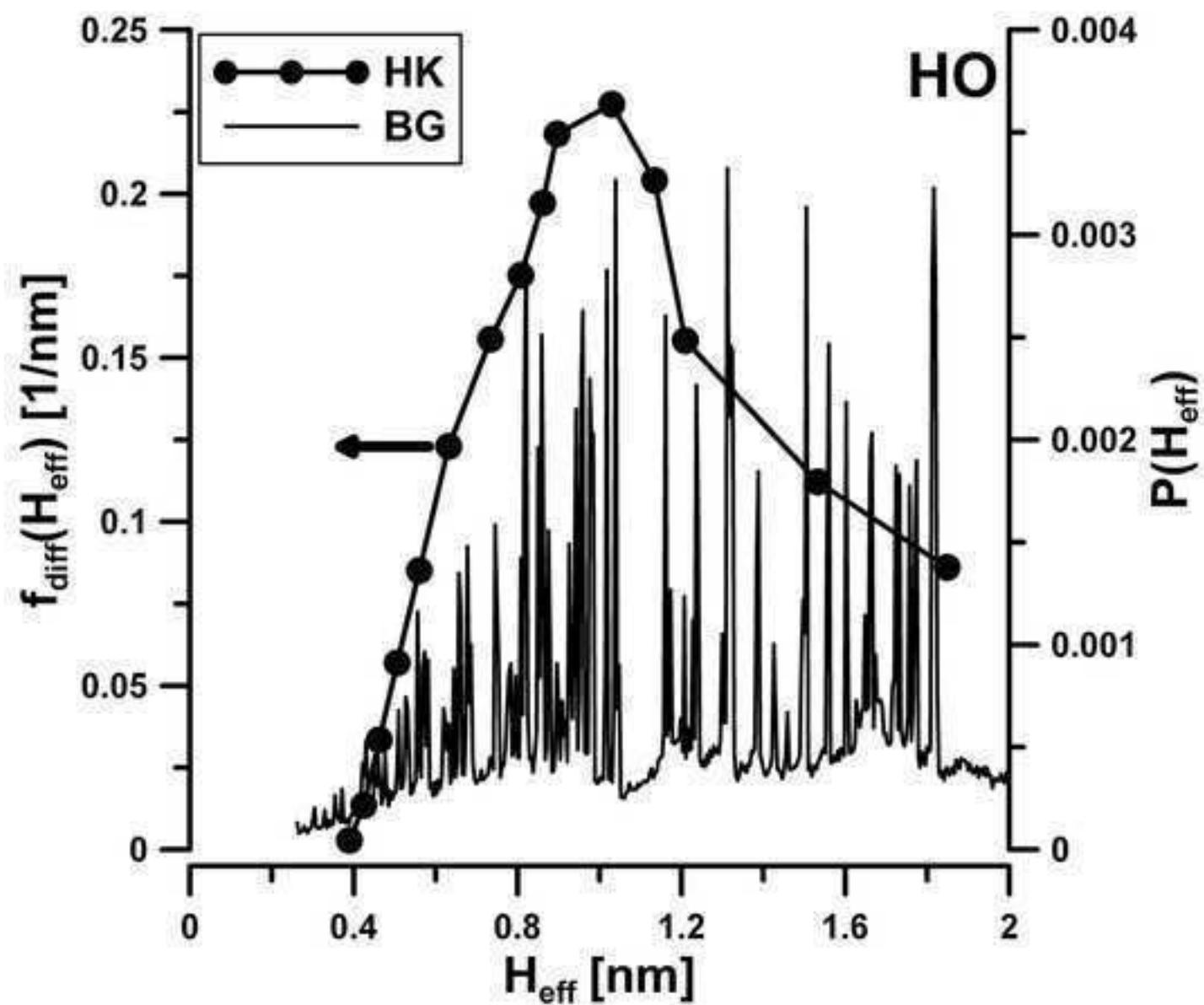


Fig. 14