Detection of ring and adatom defects in activated disordered carbon via fluctuation nanobeam electron diffraction

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Abstract

How the structure of disordered porous carbons evolve during their activation is particularly poorly understood. This problem endures primarily because of a lack of high-resolution three-dimensional techniques for the characterisation of amorphous and highly disordered structure. To address this, we demonstrate the measurement of the three-dimensional pair-angle distribution function using nano-diffraction patterns from high-energy electrons. These rich multi-atom correlations were measured for a disordered carbon and clearly show the structural evolution during activation. They provide previously inaccessible bond-angle information and direct evidence for the presence of ring and adatom defects. We observe an increase in the short-range order and the number of five-fold ring defects with activation, indicating stress relaxation by increasing curvature. These observations support models of disordered porous carbons based on curved graphene networks and explain how large amounts of free volume can be created with surprisingly small changes in the average ratios of tetrahedral to graphitic bonding.
There are currently high levels of interest in activated carbons as a cheap and readily prepared material for gas sequestration \[1\], sieving \[2\], catalysis \[3\], supercapacitors\[4\], hydrogen storage \[4\] and lithium-ion batteries \[5\]. Activation of non-graphitizing carbons results in a structural transformation that produces an increase in the carbonaceous skeleton density by \(\approx 25\%\) to up to \(\approx 93\%\) of the value of graphite and a concomitant bulk density decrease of \(\approx 20\%\)\[6\]. The atomic level structure of the carbonaceous skeleton and the processes that mediate the large structural changes during activation are not well understood, but these are critical for many applications, such as electrochemical processes \[7\]. Raman spectroscopy suggests that structural changes that occur at elevated temperatures \(800^\circ C - 2400^\circ C\) are mediated by mobile defects but the nature of these defects could not be identified \[8\].

Early structural models for these carbons based on x-ray diffraction measurements and high resolution transmission electron microscopy (HRTEM) characterised the initial structure in terms of basic structural units which were laterally confined stacks of graphitic planes. As the path to graphitization was followed, these planes could align and give rise to extended local molecular order. The state of the carbon could be adequately described by two parameters that quantify the extent of the order parallel and perpendicular to the basal planes \[9, 10\]. More sophisticated atomic modelling tools resulted in the proposal of models with greater atomic-level detail \[11\], for example, negatively-curved graphene sheets or schwarzite structures \[12\], graphene sheets with inter-plane defects resulting in curvature \[13\], or with out-of-plane defects \[37\]. A recently proposed “amorphous graphene” model, developed using \textit{ab initio} methods and experimental constraints, consists of a three-dimensional network of curved graphene sheets with a small percentage (11%) of sp\(^3\) hybridized carbons connecting the sheets and a few sp hybridized carbons \[14\]. Evidence in support of curved graphene models has been obtained from TEM images of very thin structures \[15\].

Despite the development of these many structural models that show good consistency with diffraction data, it is still not possible to claim a structural solution for these complex, disordered materials. In short, this is because conventional imaging and diffraction methods all have limitations that impede the solution of amorphous structures.

While advancements in electron aberration correction now enable routine sub-Ångstrom resolution, the interpretation of representative images of disordered porous carbons is still hampered by the projection problem, which produces images of overlapping atoms and structures \[16\]. Similarly, atomic resolution tomography is now accurate for nano-crystals \[17\], but has not yet been experimentally realized for disordered materials. For disordered materials the statistical pair correlations that can be obtained from large volume
diffraction measurements do not uniquely specify the three-dimensional structure [18, 19]. Fluctuation
scattering methods have been developed to push beyond the limitation of conventional scattering techniques
of disordered matter [20, 21, 22]. These techniques use focused, x-ray or electron beams to illuminate a small
number of local structures per measurement and collect large ensembles of data from independent sample
regions. The statistical variations in these large datasets are sensitive to the local many body correlations in
the material. Originally fluctuation electron microscopy (FEM) produced a one-dimensional curve sensitive
to higher order statistics to compliment the pair statistics [23]. Further advances have been made in detecting
local angular symmetries [24] and mapping their distribution in amorphous solids with electron nanobeam
diffraction [25].

Diffraction patterns from an amorphous material using a small probe encode a wealth of structural infor-
mation. A recent theoretical advance has shown how the averaged angular correlations from such diffraction
patterns can be transformed to a three-dimensional, real-space distribution showing the multi-atom corre-
lations in terms of angle and distance, called the pair-angle distribution function (PADF) [26]. Here we
demonstrate the capability of the PADF to distinguish between the structures of a non-graphitizing carbon
along the activation pathway. The exquisite sensitivity of the PADF to different local structures enabled the
detection of differences in the structures which remained hidden through previous characterisation methods
[6, 8].

As shown in Fig. 1(a), the PADF is obtained experimentally by first calculating an angular intensity
correlation function (see Supplementary Section S3) from an ensemble of nanobeam diffraction patterns
measured at different locations on the sample [22, 27]. The PADF is produced by transforming the angular
intensity correlations from reciprocal space into real-space to facilitate a clearer interpretation of the struc-
tural information in terms of the correlation functions in statistical mechanics. Explicitly, the PADF is a
3D distribution of local two-, three- and four-atom arrangements and takes the form:

$$
\Theta(r, r', \theta) = \tilde{g}_2(r, r' = r, 0) + \tilde{g}_3(r, r', \theta) + \tilde{g}_3(r, r', \pi + \theta) + \tilde{g}_4(r, r', \theta). \tag{1}
$$

Here $r$ and $r'$ are the inter-atomic distances of two pairs of atoms (which may share a common atom) and $\theta$ is
the relative angle between the two atom pairs [see Fig. 1(b)]. The tilde notation $\tilde{g}$ indicates that these terms
are modified from the standard atomic correlation functions $g_n$ of statistical mechanics (see Supplementary
Section S4 and Ref. [26]). The PADF is a three-dimensional distribution rich in information. It contains
peaks at values of \( r, r', \) and \( \theta \) that can identify the presence of local structures in a disordered material. The line \( \Theta(r = r', \theta = 0) \) reflects the radial distribution \([26]\). We validated the PADF analysis with a test dataset of electron nanodiffraction patterns from gold-palladium nanoparticles which produced real-space angular peaks at the expected locations for the three- and four-atom arrangements of an face-centered cubic (fcc) lattice [See Supplementary Section S5].

We collected electron nanodiffraction patterns from an unactivated and an activated disordered carbon using an 80 keV, 2.4 nm (FWHM) aperture-limited probe in an aberration-corrected scanning transmission electron microscope (S/TEM) (see Supplementary Sections S1 and S2). The carbons were obtained from a furfuryl alcohol (FA) precursor which was polymerised and then carbonised. The resulting char was ball-milled and sieved to obtain powder particle sizes of less than 100 \( \mu m \). The powdered material was activated using a cyclic O2-activation protocol that involves repeated application of a cycle in which oxygen is first chemisorbed onto the carbon at 250 \( ^\circ C \) and then removed along with some of the carbon (mainly as CO and CO\(_2\)) at 800 \( ^\circ C \) in an inert atmosphere. The unactivated char and a sample corresponding to 45% conversion were prepared for further TEM analysis (see Supplementary Section S1). This activated carbon has been investigated previously for its adsorption properties [28, 29, 30, 31] and it has a measured pore size of 0.58 \( \pm 0.02 \) nm [32].

The carbons were previously investigated using a multi-modal analysis of pycnometry, electron-energy loss spectroscopy, FEM, and x-ray diffraction [6]. This study found that both the specimens were highly \( sp^2\)-bonded and that activation increased the \( sp^2\) fraction by only a few percent. During activation the carbon skeleton densified. X-ray diffraction and FEM indicated that the in-plane correlation lengths increased and the study called this process "graphenization" [6]. Further study along the thermal annealing pathway using Raman spectroscopy suggested these structural rearrangement processes at high temperatures were mediated by point defects [8].

Results from the present analysis are shown in Fig. 1. Figure 1 c) shows a raw diffraction pattern and part d) shows a \( q = q' \) cut through the derived angular autocorrelation function from the ensemble of diffracted patterns of the unactivated specimen (see Supplementary Material Section S3). This q-space correlation shows the strong angular variations that encode the three- and four-body statistics [33], but is difficult to interpret. When transformed into the real-space PADF, numerous angular peaks are observed that can be immediately interpreted in terms of the short-range order as shown in Fig. 2.

Figure 2 displays the \( r = r' \) PADF cross-sections of the unactivated and activated specimens. In the
unactivated sample we observe structure up to 3 Å. The striped structure at distances > 3 Å is characteristic of noise surpassing the signal and has an indicative periodicity that is consistent with the maximum angular frequency used in the data analysis. These patterns were obtained using a traditional scintillator coupled CCD camera, with a modest detector quantum efficiency. New camera technology based on direct detection [34] will overcome this limitation for future studies.

The magnitudes of the activated peaks are generally higher than the unactivated indicating an enhancement of the short-range order along the activation pathway. This result cannot be explained by an increase in sample thickness, because the average intensity per pattern does not follow the same trend and the areas probed were controlled to have a comparable thickness (see Supplementary Section S3). The breadth of features in $r$ and $\theta$ from both specimens indicates a high level of variation in the local environments of atoms.

The PADF plots indicate that, in general, the short-range order persists along the activation pathway, as most peaks < 3 Å are common to the unactivated and activated samples. Many of the peaks occur in positions expected by six-fold rings (labelled G1-G4 in Fig 2) consistent with the predominantly sp$^2$ bonded structure. However, there are several further peaks that are not predicted by defect-free graphene sheets. After reviewing defect structures that are predicted and observed in graphene and graphite, we have found that five-fold rings (labelled P1, P2 in Fig 2) and three adatom positions [35] (position A, position B and dumb-bell) predict peaks closest to those observed. The adatom positions shown have comparatively lower predicted energies than other adatom positions studied in Ref. [35]. The types of adatom defects are consistent with previous studies of defects in graphene [36] and activated carbons [37]. The peak associated with B1 and D1 shifts down and becomes more defined as the specimen is activated, indicating that while such inter-plane defects are stable, they move closer to the locations expected from the model structures with further treatment. This is consistent with the removal of high energy adatoms during activation.

There is further evidence for pentagon defects in the correlation between the sp$^2$ bond distance and 2.3 Å shown in Fig. 3(a) and (b). This highlights the major advantage of PADF analysis: resolving angular signatures of local structures, i.e. 5-fold rings, that cannot be distinguished from the radial distribution function, which lacks information about local orientation. Additionally, the radial signature of 5-fold rings cannot be resolved from the first peak in the x-ray radial distribution function which has a full-width half-maximum of 0.4 Å [6], the breadth of which likely originates from the intrinsic structural complexity of the sample and not instrumentation. The presence of five-fold rings is consistent with the local curvature expected in
non-graphitizing carbons. We see that the intensity of the peak associated with in-plane pentagons increased with activation. This indicates that graphene-plane curvature is key to the opening up of free volume in the more fully activated specimen.

Models of ring defects are frequently predict distortions from regular polygon structures (i.e. ideal pentagon structures) [35]. The PADF measures the distribution of these structures and distortions may broaden or shift the location of PADF peaks (for an example based on an atomic model see Supplementary Section S8). In the first instance, comparison of the PADF to ideal regular rings facilitates identification of these defects in the material. In the future, improvements in the accuracy of PADF measurements and in the analysis of the PADF are expected to yield further information about the distribution of distorted structures.

The angular peaks of seven- or eight-fold ring defects are not distinctly resolved in Fig. 2, but may be present in the broadening of angular peaks. The bond angles of ideal heptagons and octagons are in the range 45°-52° and our observed bond angle peaks extend to this angular range. Further angular peaks are expected in vicinity of \( r = r' = 2.6 \, \text{Å} \) and \( \theta = 50° \), where there is positive correlation in Fig. 2, but this is less clear than the five-fold ring peaks.

For completeness we have marked the positions of any diamond peaks that could correspond to features in the carbon PADFs in Fig. 2. However, we note that the peaks due to tetrahedral short-range order at \( r = 1.54 \, \text{Å} \) cannot be resolved separately from the dominant \( sp^2 \) bond angle peak and peaks at distance \( r = 2.95 \, \text{Å} \) not resolved due to noise.

Multi-atom correlations in real space help significantly to complete the story of how the carbon structure alters during activation. In common with previous investigations we see that the dominant bonding is \( sp^2 \), but the PADF shows that the local order in graphene sheets is not perfect but contains many in- and out-of-plane atomic defects. The angular PADF peaks due to hexagons show closer agreement to their expected positions after activation. Activation increases the number of 5-fold rings. This is the first direct observation of this increase and is key to understanding the nature of these carbons. This observation indicates graphene sheets can adopt lower energy in-plane configurations with activation and increase curvature to release stress. This results in an increase in 5-membered ring defects and greater curvature and concomitant increase in open volume as observed experimentally. It is remarkable that despite seemingly minute changes in average bonding the structure can evolve with activation to a material having three times the accessible open volume and 1.2 times the skeleton density of its parent compound [6].

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The PADF is a rich, continuous 3D distribution and it will take further work to unlock all the information it contains. Here we have focused on the most readily interpretable information, namely the angular peak positions and changes that occur with activation. We have shown that \( \approx 1000 \) electron diffraction patterns are sufficient to measure bond-angle information and short-range order for highly complex systems that contain varying degrees of both short and medium range order. The collection of larger datasets could improve resolution and provide access to angular structure at larger length scales (i.e. \( r, r' > 3 \text{Å} \) for the non-graphitizing carbons). Electron beams are ideally suited to PADF analysis on amorphous solids at atomic length scales, but we envision the application of PADF analysis to thicker nanomaterials with x-rays to reduce the impact of absorption and dynamical scattering. We note that dynamical scattering does not impact the peak positions in pair distribution analysis [38] and our results for gold-palladium nanocrystals [see Supplementary Section S5] indicate this holds true for the angular peak locations in PADF analysis. Further detailed studies combining simulation and experiment are needed to quantify the impact of dynamical scattering. This is a non-trivial task for non-graphetizing solids, which require large and realistic structural models to aptly describe the long-range disorder and strongly covalent short-range order.

Reliably measuring angular correlations of atoms from diffraction data constitutes a significant advance in the ability to characterize numerous technologically relevant highly disordered materials. There is further scope to develop PADF analysis quantitatively by exploring the data requirements to improve resolution and convergence. Quantitative PADF analysis can potentially be used to validate molecular dynamics simulations which are frequently studied to characterise locally disordered structure, e.g. via bond orientation parameters, en route to identifying microscopic explanations for macroscopic properties. Reverse Monte Carlo modelling uses the pair distribution function as input to structure refinement [39] and could be extended to incorporate PADF fits for greatly reducing structural ambiguity. For example, similar fitting of fluctuation electron microscopy data has provided insights to support the long contended existence of paracrystals in amorphous silicon [23], although the modelling of four-body correlations and medium range order is computationally intensive. Computationally efficient bond angle constraints for nearest neighbours [40] have been demonstrated to be particularly effective for statistically reconstituting the structure of ab-initio models of glass in a recent reverse Monte Carlo benchmark study [41]. Hence we expect that the experimentally accessible angular correlations in the PADF can be readily exploited to efficiently refine the short range order for a variety of disordered solids. Different materials and length scales could be opened up by employing neutrons and x-rays [26]. This first demonstration with electrons is an initial step toward
opening up this new paradigm for disordered materials characterization.

We view the PADF technique as complimentary to existing techniques that characterise ensemble structure, such as Raman spectroscopy. Raman spectroscopy accesses local structure indirectly because the interpretation of Raman spectra requires knowledge of electronic structure and collective dynamics. Identification of individual defect types giving rise to the Raman D-band in defective graphene and graphite is challenging [42]. Raman has been used on these carbons previously [8], but this failed to identify the atomic level defects that mediate the structural changes during activation. The PADF permits the direct identification of defects by their three-body angular correlations, which can be used in combination with Raman measurements to pin down structural models.

Access to local orientational order via the PADF revealed the subtle atomic-level details of structural evolution as a non-graphitizing carbon is activated. Activation did not result in a change in the nature of the order, which for both specimens was largely sp\(^2\), but it did change the degree of in-plane ordering as was observed from an increase in the magnitude and sharpness of peaks in the PADF for the activated specimen. Specifically, activation reduced the number of high energy out-of-plane defects and increased the number of 5-fold ring defects. The second observation is a strong indicator for increased graphene sheet curvature that explains how open volumes are generated through activation even though this is accompanied by such small changes to the type of local order in the carbonaceous skeleton. These insights into the structural change during the initial stages of activation will help tune the processing of such carbons to different applications for molecular sieving [2], gas storage [1], catalysis [3], hydrogen storage [4] and lithium-ion batteries[5].

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Figure 1: (a) The experimental set up. A nanofocus electron beam is scanned over the sample and an ensemble of diffraction patterns are measured. The diffraction patterns are used to compute an intensity correlation function, which is transformed finally into the 3D real-space PADF. (b) The coordinates of three-body and four-body arrangements that are measured by the PADF. (c) A raw electron nanodiffraction pattern from the carbon sample. The shadow on the left side is the beam stop that is required due to the limited dynamic range and detector quantum efficiency of the charge coupled device (CCD) camera. (d) A 2D cross-section of the intensity correlation function calculated from the ensemble of unactivated carbon data.
Figure 2: The 2D cross-section through the measured PADF functions $\Theta(r, r', \theta)$ where $r = r' \text{ Å}$ is shown for the activated and unactivated carbon char. Selected angular peaks predicted by various short-range structures are marked in black symbols as follows: hexagon symbol for in-plane graphite; pentagon symbol for 5-fold rings; round symbol for heptagon peaks; upward triangle symbol for adatom position A; downward triangle symbol for adatom position B; cross symbol for dumb-bell; and diamond symbol for diamond lattice. Atomic models are shown for numbered labels. The labels ‘G’, ‘Gra’ and ‘Dia’ denote graphite in-plane, graphite out-of-plane and diamond respectively. The white symbols indicate peaks generated by the PADF’s reflection symmetry around 90 degrees. Note $\Theta(r, r', \theta)$ has been scaled by $r^2$. 

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Figure 3: (a) Line plots through $\Theta(r, r', \theta)$ for $r = 1.4$ Å and $r' = 2.3$ Å that further support the presence of pentagon defects. (b) Line plots through $\Theta(r, r', \theta)$ for $r = r'$ and $\theta = 0$. The vertical lines correspond to the nearest-neighbour separation (1.5 Å), the pentagon second neighbour separation (2.3 Å) and graphite interplane separation (3.3 Å) rounded to one decimal place. The activated data shows significant increase in short range order. Note $\Theta(r, r', \theta)$ has been scaled by $r^2$. 
Author Contributions: M.B. and C.H. fabricated the carbon samples. A.L., E.B. and M.W. collected the nanobeam diffraction data. A.M. designed the PADF analysis and wrote the PADF analysis code. A.M. and E.B. analysed the data. A.M., A.L. T.P., E.B. interpreted the results. A.M. and A.L. wrote the manuscript with contributions from all authors. Competing Interests: The authors declare no competing interests. Data and materials availability: PADF analysis code is available on github (https://github.com/amartinrmit/py2PADF.git). Data is available from Figshare (figshare.com).

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