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Pattern recognition approach to quantify the atomic structure of graphene

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We report a pattern recognition approach to detect the atomic structure on high-resolution transmission electron microscopy images of graphene. The approach provides quantitative information such as carbon-carbon bond lengths and bond length variations on a global and local scale alike.

Graphene is considered a key material for future electronic applications with the possibility of very high performance transistors [1], spintronics [2] and ballistic devices even at room temperature [3]. The degree to which the actual performance of graphene devices can live up to the theoretical predictions depends critically on the presence of defects, atomic configuration of edges. In essence, any deviations from perfect lattice periodicity can be important, which for instance is manifested in the sensitivity of electronic properties to strain [4].

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Transmission electron microcopy (TEM) in general and high-resolution TEM (HRTEM) in particular can provide information about the atomic structure and defect landscape of graphene [5]. While important parameters like the carbon-carbon (C-C) bond length are possible to determine, this is usually done manually in small areas [6], due to time-consuming work of manually analyzing the HRTEM images. Here we describe a method for fast, automatic structure detection in graphene in a large number of sequentially acquired HRTEM images. The method enables quantitative information such as C-C bond length or bond length variations to be determined from images in a fast and reliable way, and can be used on many images to allow access to this information from a large area.

Suspended single-layer graphene synthesized by chemical vapor deposition (CVD) (Graphenea, Spain) or by mechanical exfoliation of graphite [7] and transferred to TEM grids have been investigated using the automatic method. The graphene is imaged using a FEI Titan 80-300 Environmental TEM (ETEM) equipped with a monochromator at the electron gun and a spherical aberration (C_S)-corrector for the objective lens. All images are acquired with the microscope operated at 80 kV, which is below the knock-on threshold of carbon atoms in pristine graphene [8]. In order to optimize the imaging conditions and thereby the input for the structure detection, the electron beam energy spread was reduced to below 0.3 eV using the monochromator, while the C_S corrector was aligned to minimize the spherical aberration C_S. These conditions result in a resolution better than 0.12 nm, allowing us to resolve the 110-reflections of graphene and visualize the atomic structure accurately. The images are recorded using a Gatan US1000 CCD camera with an exposure time of 1 s.

The structure determination algorithm involves several steps. Utilizing Fourier transformation and local maxima detection, the mean graphene structure over the whole image is detected and used as starting point. The basis is a triangular lattice (triangulation) with a side length of roughly 0.247 nm, connecting three hexagonal centers (nodes) of the graphene structure. Hexagon center positions in the image are recognized as contrast extremes, minima for negative C_S or maxima for positive C_S. Nodes and triangles are removed from the triangulation when the local contrast properties or

geometry deviate significantly from the expectations, and consequently areas like holes or amorphous material can be automatically omitted. In a final step, the node positions are adjusted by grid matching [9]. These steps enable a full reconstruction of the atomic structure of the observed graphene area in most cases. A more detailed description of the algorithm will be published elsewhere.
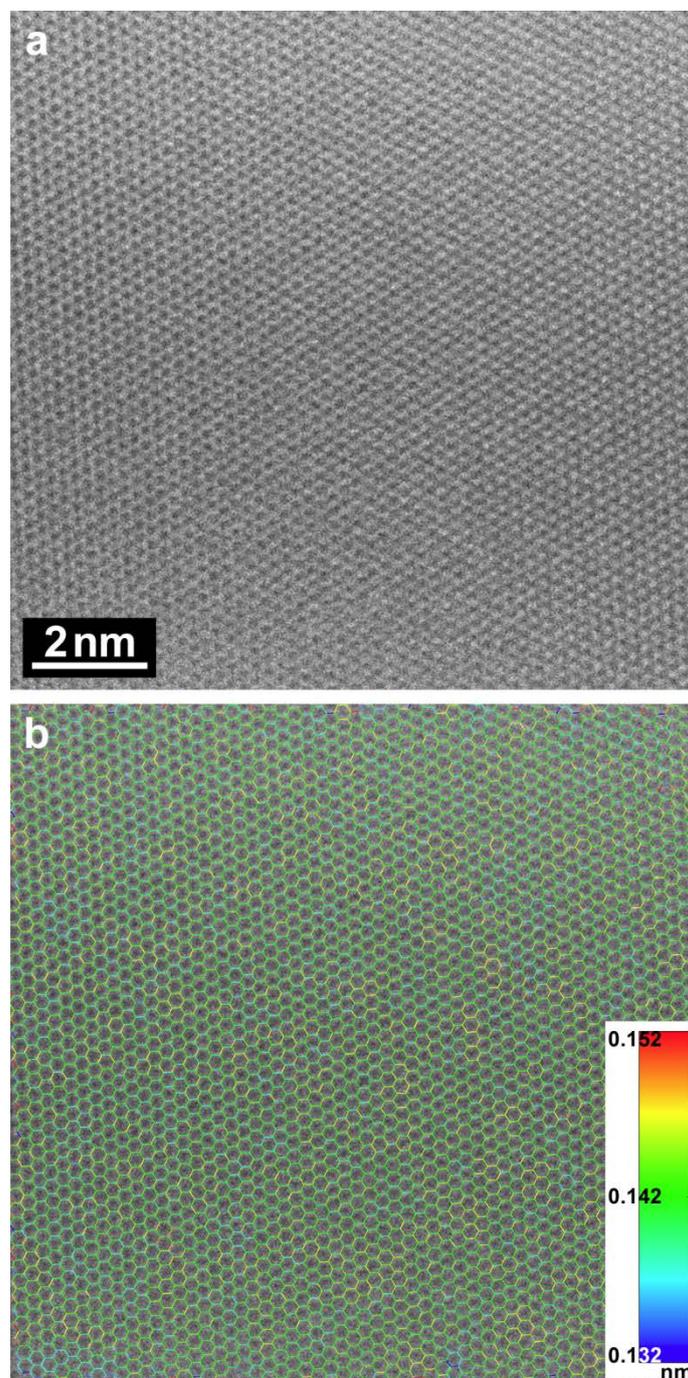
Figure 1: Pristine graphene. (a) HRTEM image, (b) image overlaid with the detected and reconstructed graphene structure. The color coding represents the C-C bond lengths. A homogenous distribution of bond lengths is observed.
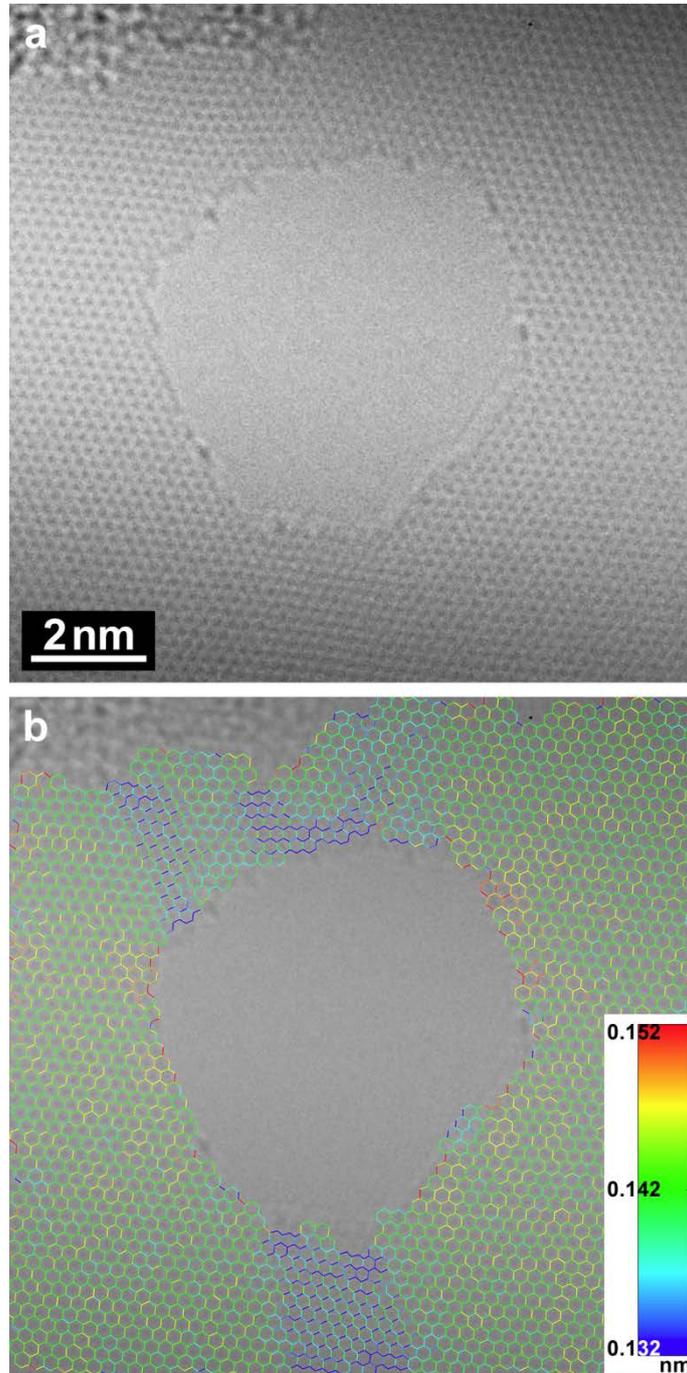
Figure 2: Graphene with a hole, formed under the influence of the electron beam. (a) HRTEM image, (b) image overlaid with the detected and reconstructed graphene structure. Color coding is the same as in Fig. 1b. Significantly shorter bond lengths with preferred orientation are observed above and below the hole.

Figures 1a and 2a show HRTEM images of two different areas of graphene. The hexagonal honeycomb lattice is easily recognized. Using negative Cs imaging, the carbon atoms are bright spots, with the centers of the hexagons appearing dark. In Fig. 1a, a hole in the graphene, formed

1 under the influence of the electron beam is observed. Due to the inherent small signal-to-noise

2 (S/N) ratio in the graphene image [5], as well as the continuous beam induced changes of the atomic

3 structure at the edge [10], the termination of the hole cannot be completely resolved. Nevertheless, a

4 predominant zigzag termination is assumed, which is in agreement with previous findings [11]. In

5 Fig. 1b and 2b, the reconstructed graphene structure determined from the algorithm is overlaid,

6 showing the actual hexagonal lattice of the graphene. The color coding represents the C-C bond

7 lengths. As the absolute value retrieved from the images is dependent on the imaging conditions and

8 the calibration, only the relative change within an image is considered. Figure 1b, representing a

9 pristine area, gives the impression of a homogenous distribution of bond lengths. This is reflected in

10 the bond length histogram (Fig. 3 red) which exhibits a normal distribution.
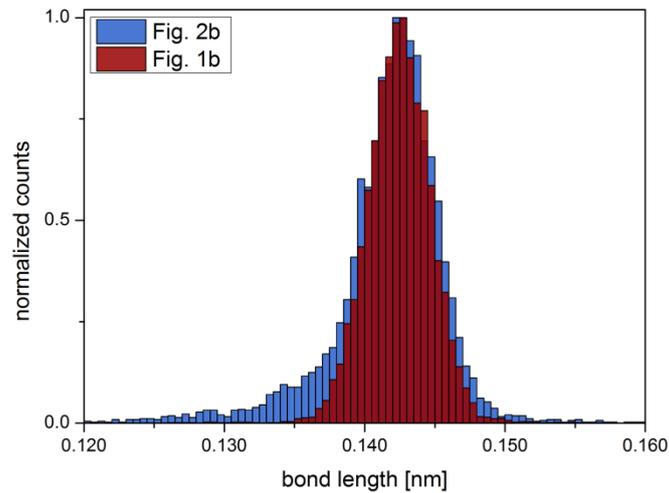
11

12 **Figure 2**: Histograms of the detected bond lengths from Fig. 1b (red) and Fig. 2b (blue). The bond

13 lengths are binned by 0.5 x 10^{-3} nm steps; the counts are normalized for simpler shape comparison

14 between the two histograms. The red histogram shows a normal distribution. The blue histogram

15 exhibit a tail towards shorter bond length.

16

17 For the case of a defective structure, as in Fig. 2, the algorithm detects nearly all graphene

18 hexagons. The only exceptions are structures close to the hole and the edge termination itself, which

19 most likely is due to insufficient imaging conditions, as mentioned above. The area of amorphous

20 carbon from the transfer process or synthesis (top left) was disregarded manually, but the area of the

hole is detected by the algorithm and automatically left out in the analysis. A homogenous distribution of bond lengths is observed to the left and right of the hole. For the areas above and below the hole, significantly shorter bond lengths are detected. This is obvious in the histogram as well (Fig. 3 blue), where a tail towards shorter bond length is visible. Suspended graphene is known to form out-of-plane ripples [12], which are expected to have a lateral size of 2 – 20 nm and a height of 0.2 – 1 nm, with an inclination of ≈5° from the horizontal flat sheet. In this case, the projection of the bond length is measured from the image, making the lengths appear shorter. The shortest observed bond lengths above and below the hole have a preferred orientation, almost horizontal in this image. This may be explained by the graphene sheet being slightly folded, as this should lead to a change in z-height as well as elastic deformation and strain mainly in the direction perpendicular to the fold, as we observe in the image. For an almost flat sheet, these bond lengths would represent a strain of about 7 – 8 %; a pure inclination without bond length change would give an angle of about 22° between the two adjacent carbon atoms and an offset in height of about 0.05 nm. The rearrangement and knock-out of carbon atoms under the electron beam at the edge of the hole [10] can lead to structural deformation as well. A combination of both, a real shorting of the bond length and an artificial shortening due to projection in the image, is the most realistic explanation of our finding. It is important to notice, that even though the shorter bond lengths are represented in the global histogram, the local information, where these bonds actually appear in the structure, is only available in the image itself. The acquired local information in the bond length indicates a possible correlation between measured short bond lengths and folding of graphene. The nature of the bond length shortening will be clarified in a future study.

The automated structure detection for quantitative information extraction from high-resolution TEM images is possible for a large amount of images at relatively low time-cost and minimum manual interaction, making it easier and more feasible to follow structural changes in a series of images. Incremental and time dependent structural changes caused by either electron beam induced effects and/or external stimuli like temperature, current etc. can be monitored and quantified in future investigations in greater depths than standard image analysis procedures allow.

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