Examining the Edges of Multi-Layer Graphene Sheets

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Multi-layer graphene (MLG) sheets were produced from highly ordered pyrolytic graphite by mechanical exfoliation. We use aberration-corrected, low-voltage, high-resolution transmission electron microscopy to study the atomic structure at the edges of the sheets. In general, we find two different types of edges of MLG sheets are produced, either parallel to a zigzag direction or an arm-chair direction. A MLG sheet with edges parallel to the zigzag direction was observed to have small random corrugations and was relatively straight. We observed edges parallel to the arm-chair direction with highly corrugated atomic structure and terracing. We show that the corrugations are due to sawtooth oscillations in the atomic structure with zigzag edge terminations along the general arm-chair direction.

Interest in graphene and multi-layer graphene has been driven by the remarkable electrical[1−3] and mechanical properties.[4] The electronic[5] and magnetic[6,7] properties of graphene is expected to be influenced by the nature of the carbon atoms at the edges. Electrostatic gating of graphene devices can result in transitions from p- to n-type that occur inhomogeneously throughout the sheet with p-type conducting edges.[8] Zig-zag graphene ribbons are predicted to have a spin-polarized ground-state that is susceptible to loss of spin polarization by the presence of defects at the edges.[9] Characterization and understanding of the edge atomic structure and termination in graphene and multi-layer graphene sheets is an important step toward future tailoring of the electronic and spin dynamics through controlled edge terminations. Information regarding the structure of the intrinsic edges of graphene and MLG sheets produced via exfoliation is relatively unknown and further work is needed to build up an understanding.

Tapaszto et al. recently demonstrated the ability to engineer the electronic structure of graphene by forming nanoribbons using scanning tunnelling microscope lithography with nanometer precision to control the edge structure.[10] Etching of graphene and MLG sheets represents one possible technique to control the crystallographic direction of the edges. Datta et al. recently showed Fe particles etched channels along specific crystallographic orientations in monolayer graphene when annealed in the presence of hydrogen.[11] A similar cutting effect was also demonstrated by Ci et al. using Ni nanoparticles.[12] Sawtooth edge terminations in graphene nanoribbons are predicted to lead to richer band gap features than straight edge terminations.[13] Developing methods to control the edge termination in graphene and MLG sheets suspended in solution may enable advances in ensemble spin resonance measurements and elucidate the dynamics of magnetization.

Here we examine the structure of the edges of the MLG sheets in order develop an understanding of the intrinsic edge termination. We prepared multi-layer graphene sheets suspended in solution using a simple exfoliation method and develop insights into the cleavage process. The edges are characterized using low-voltage, aberration-corrected HR-TEM at 80 kV in order to limit the knock-on damage and to determine the relative zigzag and arm-chair orientations. Multi-layer graphene sheets are produced using a razor to slice flakes from the side of a highly ordered pyrolytic graphite (HOPG) block, parallel to the *c*-axis. This resulted in a fine black powder, which was then added to vial containing 1,2-dichloroethane and sonicated for 10 min. The solution was then left for 10 min, allowing large aggregates to settle to the bottom of the vial. A lacey carbon-coated TEM grid was then dipped into the top region of the solution. Multi-layer graphene sheets attach to the lacey coated TEM grid upon drying of the 1,2-Dichloroethane. HRTEM was performed using an FEI Titan[3] microscope with third-order spherical aberration correction at 80 kV. Angstrom spatial

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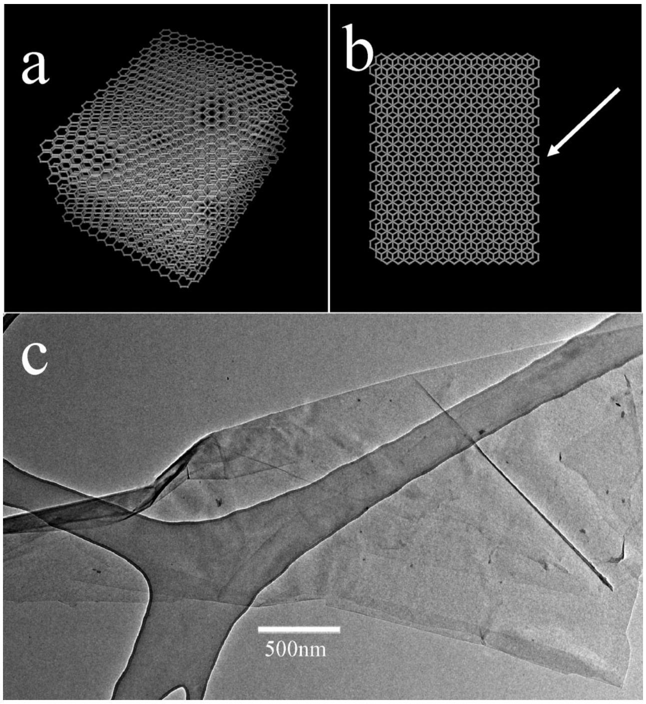

Figure 1. (a) Schematic illustration of a rectangular block of HOPG, (b) schematic illustration of top view of HOPG block with the cutting direction indicated with an arrow, (c) TEM image of an exfoliated multi-layer graphene sheets on a lacey carbon grid.

resolution was achieved and enabled the atomic structure of the carbon atoms to be directly imaged.

Figure 1a shows a schematic illustration of a rectangular block of HOPG. Figure 1b shows the schematic illustration of the top-down view of the HOPG block. A sharp clean razor was used to slice along the side of the HOPG block parallel to the *c*-axis, indicated with an arrow. Large pieces of graphite were also observed within the sample; however, they were not studied because they were too thick. Instead, we focus on the large number of smaller sheets of graphite that are much thinner due to the reduced number of graphene sheets. Figure 1c shows the TEM image of a typical multi-layer graphene sheet on the lacey carbon-coated grid. Several folds can be seen in the MLG, which is typical in thin sheets of graphite. The diameter of the MLG sheets was generally between 500 and 2000 nm and 1−10 graphene layers thick. The weak contrast of the thin MLG sheet is apparent next to the strong contrast of the lacey carbon grid.

The presence of folds in the MLG sheets complicates the analysis of the edge structure. Folds can give rise to Moire patterns from rotational stacking faults and are also typified by long smooth straight edges.[14] Edges produced because of folding are not the true intrinsic edge of the exfoliated MLG. We examined edge regions free from folds, typified by roughness and corrugations beyond the atomic scale. The angstrom resolution of our aberration-corrected HRTEM at 80 kV enables the direct imaging of the atomic structure of the carbon atoms and allows the direction of the graphene lattice relative to the edges to be determined. We found in general that the edges of our MLG sheets were parallel to either an arm-chair or zigzag orientation of the graphene lattice.

Figure 2a shows the TEM image of a MLG sheet with a large number of edges that were parallel to the zigzag orientation of the graphene lattice. Figure 2b shows the TEM image of the region indicated with a red box in Figure 2a. We measured the angles produced by a change in the direction of the edge and found the majority were multiples of 30°. This indicates a change between the arm-chair and zigzag orientation of the edge termination. Figure 2c shows a TEM image of the region indicated with a red box in Figure 2b. A 2D fast Fourier transform was performed on this image and is shown in Figure 2d. The spots of the FFT correspond to 0.21 nm spacing and indicate the direction of the arm-chair axis in the MLG sheets (see the Supporting Information, Figure S1). A white arrow is included in Figure 2d to indicate the zigzag orientation, and we find this is parallel to the arrow in Figure 2c used to indicate the edge direction. This shows the edge is cleaved along the zigzag orientation. Figure 2e shows the HRTEM image of the region indicated with a red box in Figure 2d. The atomic structure of the MLG sheets is observed and confirms the orientation of the zigzag direction. The edge of the MLG sheet is rough and contains small scale random variations. This is attributed to the large amount of small carbon pieces that can be seen covering the surface and edges of the MLG sheets. These small pieces of carbon are most likely produced during the mechanical exfoliation procedure combined with the sonication in solvent.

The strong and weak contrast that results in the hexagonal pattern in the HRTEM image in Figure 2e is due to the corresponding overlapping of carbon atoms in the AB Bernal stacked graphene layers. This is shown in the structural representation in Figure 2f, where a black dot shows a region of increased overlap of carbon atoms and the red hexagon surrounding this shows the region of reduced overlap of carbon atoms. The black spot can have either strong or weak contrast depending on the defocus value used in the HRTEM imaging and in Figure 2e we see it as strong contrast.[14] Figure 2g shows a structural representation of a MLG sheet, which has its edge parallel to the zigzag direction (blue) and perpendicular to an arm-chair direction (orange).

We found the majority of MLG sheets contained edges that were terraced and highly corrugated. These types of edges were mostly parallel to an arm-chair orientation, opposite to the MLG edge examined in Figure 2. Figure 3a shows the TEM image of a MLG edge parallel to the arm-chair orientation. The 2D FFT is shown in Figure 3b and the arm-chair orientation is indicated by the position of the spots and the included arrow. The nature of the outermost edge of the MLG sheet in Figure 3a appears different to that of Figure 2. The edge appears corrugated, but the direction of the corrugations coincides primarily with directions of the zigzag orientation and sometimes the arm-chair orientation. Thus, there exists fine-structure in the outermost edge termination. The edge is also terraced, with successive layers thinning out toward the edge. This is seen as distinct lines of contrast and we can see that a large majority of these

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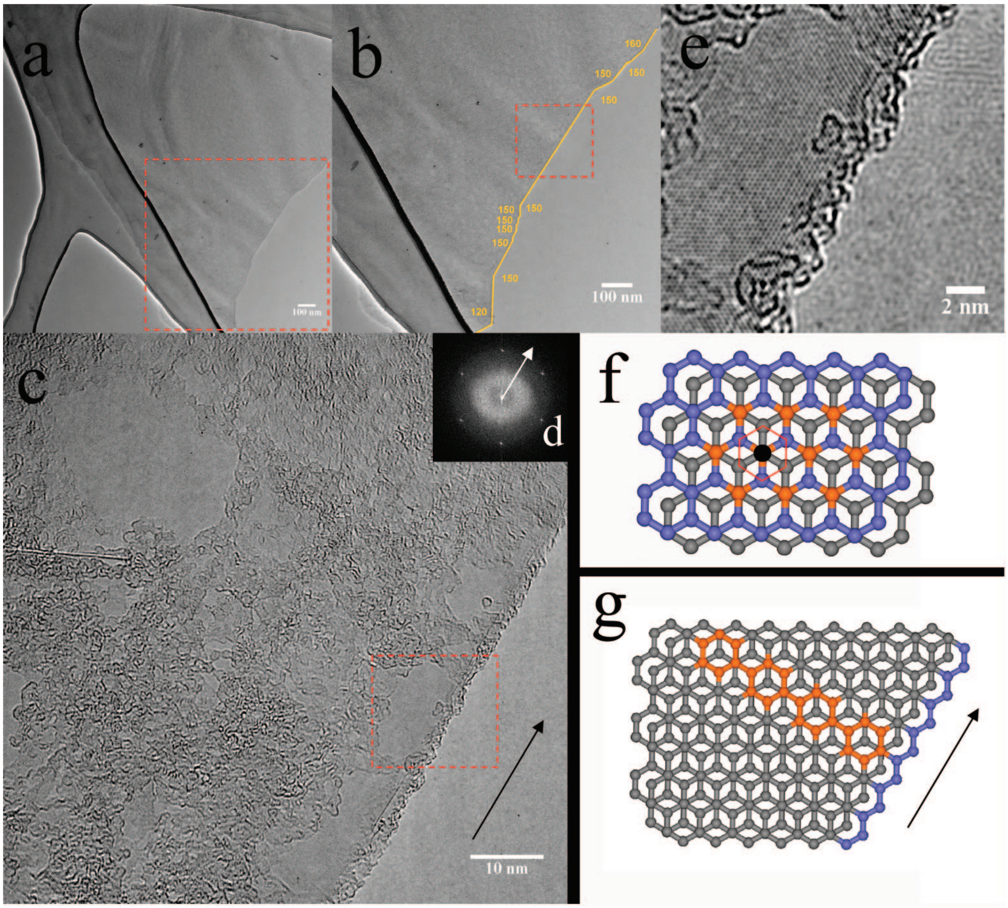

Figure 2. (a) TEM image of a multi-layer graphene sheet, (b) TEM image of the region indicated with a red box in (a), with angles measured at the edge. (c) TEM of the region indicated with a red box in (b). (d) 2D FFT of the TEM presented in (c), spots indicate direction of arm-chair orientation and arrow indicates zigzag direction. (e) HRTEM image of the region indicated with a red box in (c), showing the atomic structure and orientation of the graphene sheets. (f) Structural representation of AB Bernal stacked graphite, with red hexagon and block spot indicating the regions that give rise to strong and weak contrast in HRTEM images. (g) Structural representation of zigzag edge termination in AB Bernal stacked multi-layer graphene, with the arm-chair direction highlighted in orange and the zigzag edge highlighted in blue.

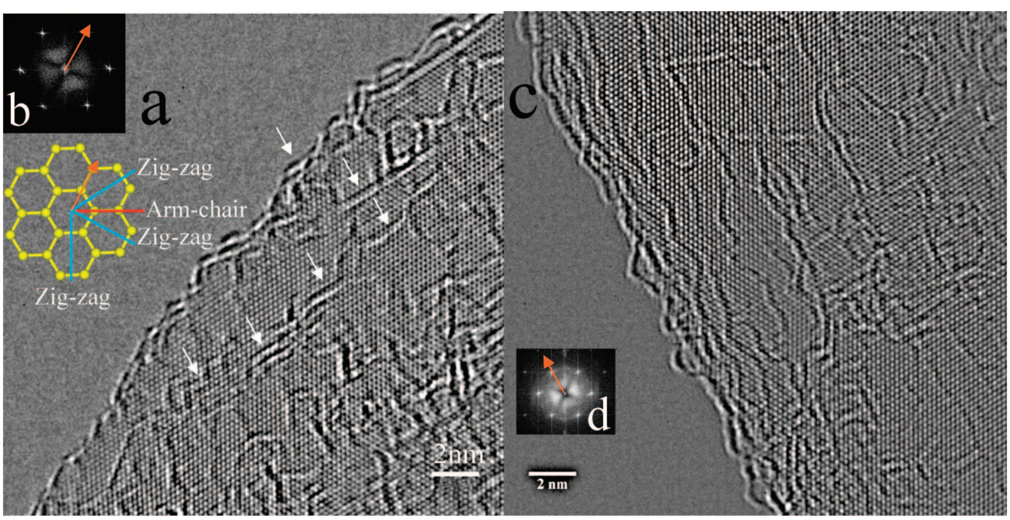

Figure 3. (a) HRTEM image of the edge of a multi-layer graphene sheet, with a schematic illustration showing the orientation of the hexagonal graphene network and the relative zigzag and arm-chair directions. (b) 2D FFT of the HRTEM image in (a). (c) HRTEM image of the edge of another MLG sheet. (d) 2D FFT of the HRTEM image in (c).

lines in Figure 3a are along the zigzag direction. Figure 3c shows another MLG sheet with similar terracing and corrugations at the edges. The FFT in Figure 3d shows the edge is also parallel to an arm-chair orientation, indicated with an arrow. A large number of the lines of strong contrast produced by terraced graphene sheets have directions parallel to the zigzag orientation.

To examine the corrugations of the edges of the MLG sheets in more detail, we found an edge parallel to the arm-chair orientation with a reduced number of graphene layers.

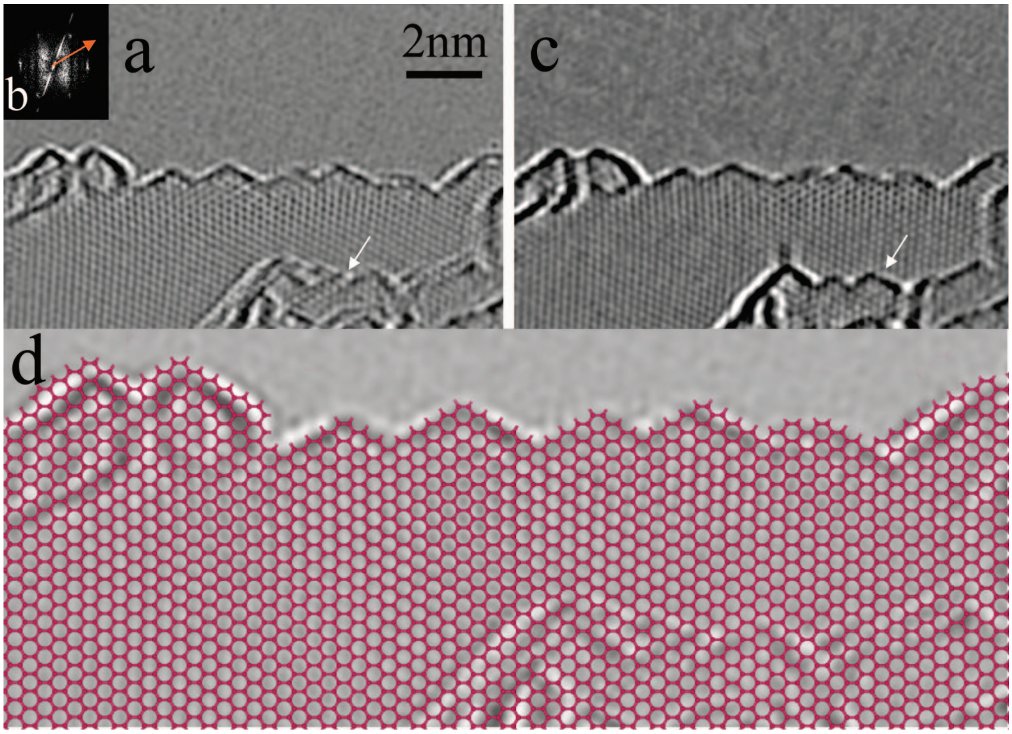

Figure 4. (a) HRTEM image of the edge of a MLG sheet. (b) 2D FFT of the HRTEM image in (a). (c) HRTEM image taken with different defocus to enhance contrast from the edge indicated with an arrow. (d) Schematic representation of the edge termination of a graphene sheet overlaid on top of the HRTEM image shown in (a).

This enabled clear HRTEM images to be obtained that revealed the details of the corrugations with high resolution. Figure 4a shows the edge of a MLG sheet with clearly defined sawtooth structure. An arrow is included to show the edge of a terraced thicker region containing more layers of graphene. Figure 4b shows the 2D FFT from Figure 4a with an arrow indicating the zigzag orientation of the graphene sheets. The orientation of the sawtooth oscillations in the edge structure correspond to zigzag directions on the graphene lattice. Figure 4a shows that even though the edge propagates parallel to the arm-chair direction, the fine structure of the edge shows termination along the zigzag orientation. Figure 4c shows the same region as in Figure 4a, but with the defocus adjusted in order to obtain suitable contrast from the edge of the terraced region indicated with an arrow. The edges of this terraced region also have sawtooth structure along the zigzag orientation. Panels a and b in Figure 4 show curvature of the lattice structure indicating some degree of bending of the MLG sheets toward the edges. Figure 4d shows a structural representation of the sawtooth zigzag edge termination overlaid on top of the HRTEM image. This illustrates how the sawtooth zigzag edge termination could be formed.

During the examination of the edge structures of MLG sheets it is very important not to modify the structure by electron-beam-induced effects. Prolonged irradiation and high electron beam current densities can lead to structural changes that will give misleading information about the intrinsic edge terminations formed during the exfoliation process. We used low-beam current densities in our TEM analysis and obtained our images before the onset of structural modification was induced. Care was also taken to reduce the processing of material. This enables the structural observations deduced from HRTEM to be directly correlated with the cleavage planes arising from the mechanical exfoliation using razor blades. We did not perform any annealing process to the MLG sheets because this would change their intrinsic structure.

In summary, we have shown that exfoliating HOPG parallel to the *c*-axis can lead to MLG sheets dispersed in 1,2-dichloroethane. Examination of the intrinsic edge structure of these MLG sheets reveals that the edges were predominantly parallel to either an arm-chair or zigzag direction. In the case where an edge was parallel to a zigzag direction, we found small random variations in the edge structure, most likely because of small carbon pieces coating the structures that were produced during the exfoliation process. In the case where an edge was parallel to an arm-chair direction, we found large corrugations with sawtooth structure along the zigzag directions. These results suggest a preference for zigzag termination of graphene in these MLG sheets.

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Supporting Information Available: Figure S1 showing how FFT analysis can be used to determine the orientation of the graphene lattice (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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