Supplementary Information for “Experimentally Engineering the Edge Termination of Graphene Nanoribbons”

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1. **Determination of chiralities of GNR segments and location of edge states**

The flat morphology of the etched GNRs and the atomically resolved STM images allow us to unambiguously determine the chirality of each segment. In Figure S1, two dashed black lines lie parallel to the edge orientation and the zigzag orientation respectively. The chiral angle between them is 19.1°, from which we determine that this segment is along the (2,1) vector of the graphene lattice. Superimposing the graphene lattice structure with the (2,1) edge orientation reveals that the STM intensity enhancement is localized along the zigzag-like fragments.

2. **Simulations of different hydrogen terminations for zigzag GNR edge**

For the zigzag GNR, there are two basic hydrogen terminations – with either one or two hydrogen atoms terminating the outermost carbon atoms. In the first case, the terminated carbon atoms have $sp^2$ hybridization and thus contribute to the π-electron network of graphene. When terminated with two hydrogen atoms, the edge carbon atoms assume $sp^3$ hybridization and do not contribute to the π-electron system. This configuration has the π-electron network topology of the so-called Klein edge. Both $sp^2$ and Klein edge terminations
give rise to edge states localized on only one of the sublattices of graphene, but in each case the sublattice is different. Simulated STM images for these two cases (calculated for the same bias voltage as in the experiment) are shown in Figures S2a ($sp^2$ case) and S2b ($sp^3$ case). These simulated images show edge states localized on different sublattices of graphene, thus allowing the two cases ($sp^2$ versus $sp^3$ hydrogen bonding) to be distinguished through comparison with experimental images. The corresponding experimental image for a zigzag edge with superimposed lattice structure is shown in Figure S2c. By observing which sublattice the experimental intensity enhancement is associated with it is possible to determine that this is the $sp^2$-bonded case and not the $sp^3$-bonded case. This provides further evidence (beyond our calculations of thermodynamic stability) that the experimentally observed zigzag edge has only one hydrogen atom per edge carbon atom.

3. Simulations of different hydrogen terminations for the (2,1) chiral edge.

The (2,1) chiral edge has 3 inequivalent positions of edge carbon atoms (see Figure S3). Thus, there are possible $2^3 = 8$ different configurations in which either 1 or 2 hydrogen atoms terminate each edge carbon atom. The simulated STM images of all 8 configurations are shown in Figure S3a – h. Only three of these configurations (Figures S3a, g, h) have regions of stability as shown in Figure 3c of the main text. Only two of them, the normal chiral edge with one hydrogen atom per edge carbon atom (Figure S3a) and the one with two hydrogen atoms terminating edge carbon atoms in position 2 and 3 (Figure S3g) qualitatively agree with the experimental STM image (see Figure 2d). These two cases are electronically equivalent since they share the same $\pi$-electron system boundary. However, the structure with two hydrogen atoms per carbon atom lies in the regime where graphene is
thermodynamically less stable than graphane (see main text), and so we conclude that the observed termination of the (2,1) chiral edge has one hydrogen atom per edge carbon atom.

4. Comparing average linescan profiles between experimental images and simulation

Here we further compare the experimental data and simulations for GNR edge electronic structure by examining average line profiles perpendicular to zigzag and armchair. We took more than 20 parallel line scans from the experimental data in the shaded regions of Figures S4a and S4b, and then averaged them to get the blue curves in Figures S4e and S4f. For the simulation images, we first used a mean-filtering image processing method to account for the finite size of the STM tip, and we then took an average of parallel line scans oriented perpendicular to the edges. The theoretical line scans obtained in this way are depicted as red dashed lines in Figures S4e and S4f, and are offset vertically for clarity.

For the zigzag edge, both the experimental and theoretical line scans exhibit an LDOS oscillation with a period of 2.1 Å, which is close to the distance between neighboring zigzag chains. This oscillation can be explained by the fact that the localized edge state decays exponentially over zigzag chains away from the edge. For the armchair edge, a different modulation period of 3.8 Å is seen. This can be explained by intervalley scattering of electrons.\textsuperscript{23} The zigzag edge is seen to have a large buildup in LDOS near the edge (in both the experiment and the simulation) which is not seen for the armchair edge. This is due to the fact that the zigzag edge has an edge state while the armchair edge does not.

Figure Captions.
**Figure S1: Determination of chiralities of GNR segments and location of edge states.** STM image of a (2, 1) chiral edge ($V_S = -0.97$ V, $I_t = 50$ pA). Two dashed black lines lie parallel to the edge orientation and the zigzag orientation respectively. The chiral angle between them is 19.1°. The green superimposed graphene lattice structure shows that the edge-state bright spots reside on the zigzag fragments.

**Figure S2: Edge termination of zigzag GNR.** Simulated STM images of (a) zigzag edge with one hydrogen atom per edge carbon atom and (b) zigzag edge with two hydrogen atoms per edge carbon atom (Klein edge). The images were simulated using a tight-binding Hamiltonian within the Tersoff-Hamann approximation. The bias voltage is the same as in experiments ($V_S = -0.97$ V). Solid lines correspond to covalent bonds between neighboring $sp^2$ carbon atoms, the green dots denote $sp^3$ carbon atoms. (c) Experimental image of a zigzag segment ($V_S = -0.97$ V, $I_t = 50$ pA) with superimposed lattice structure.

**Figure S3: Simulated STM images of different hydrogen terminated configurations for a (2, 1) chiral edge.** Electronically equivalent configurations shown in panels a and g are the thermodynamically most stable terminations (see Fig. 3c of the main text) and match the experiment. The images were simulated using a tight-binding Hamiltonian and the Tersoff-Hamann approximation. The bias voltage is the same as in experiments ($V_S = -0.97$ V). The solid lines correspond to covalent bonds between the neighboring $sp^2$ carbon atoms ($sp^3$-hybridized edge atoms are shown as green dots).

**Figure S4: Comparison of line profiles derived from experiment and simulation for GNR zigzag and armchair edges.** (a, b) Experimental images ($V_S = -0.97$ V, $I_t = 50$ pA) of (a) GNR zigzag and (b) GNR armchair edges, with blue regions showing areas where linescans were
averaged. (c) GNR zigzag and (d) GNR armchair edge LDOS simulations with red areas indicating where linescans were averaged. Average linescan profiles for the experiment (blue lines) and the simulations (red lines) are shown for (e) GNR zigzag and (f) GNR armchair edges.
Figure S3
Figure S4