Graphene Nanoribbons with Smooth Edges as Quantum Wires

Xinran Wang, Yijian Ouyang, Liying Jiao, Hailiang Wang, Liming Xie, Justin Wu, Jing Guo, and Hongjie Dai

Supplementary Information:
1. High resolution aberration-corrected TEM image of a high quality GNR.
2. Extraction of $E_g$ for the high quality GNR devices using NEGF simulation.
3. Transport data of GNR1 ($L\sim86$nm) at 4.2K in a different cool down.
4. Phase coherent transport in GNR devices.
5. Low temperature conductance of wider GNR devices.
6. Calculation of the excited states energy and comparison with experiments.
7. Simulation of Coulomb blockade pattern of GNR2 and comparison with experiments.
8. Electron transport data of a lithographic GNR.
9. Additional electron transport data of unzipping derived GNRs.
10. Raw data in Figure 3 of the main text without the dashed lines.
11. Conductance plateaus of GNR1 and GNR2 at low temperatures.
1. High resolution aberration-corrected TEM image of a high quality GNR.

Fig. S1. Aberration-corrected TEM image of a typical bi-layer, non-AB stacked GNR in the sample used for this work with apparently very smooth edge. The data was taken under an operation voltage of 80 kV on TEAM 0.5 at the Lawrence Berkeley National Laboratory. For systematic TEM and Raman data of GNRs produced by the nanotube unzipping method (ref.10 of main text), see ref. 11 of the main text.

2. Extraction of \( E_g \) for the high quality GNR devices using NEGF simulation.

The \( G-V_{gs} \) characteristics in Fig.2a suggest asymmetrical SB heights for hole and electron transport. The SB height for holes is smaller than that for electrons, and is likely to be negative. In order to extract the bandgaps from the measured minimum conductance at different temperatures, the quantum transport equation is solved in the NEGF formalism with a self-consistent potential [1] to compute the minimal conductance, in which the self-consistent potential is obtained by a three-dimensional Poisson solver. The channel conductance is computed by the Landau formula, 

\[
G = 2e^2/h \int Tr(E) \left[ -\frac{\partial f}{\partial E} \right] dE ,
\]

where \( Tr(E) \) is the transmission computed by the NEGF formalism, and \( f(E) = 1/(1+\exp((E-E_f)/k_BT)) \) is the Fermi-Dirac distribution function. The Hamiltonian is described by the Dirac Hamiltonian with quantized transverse wave vectors. The simulated ballistic conductance is multiplied by a gate-voltage- and temperature-independent transmission \( 0<T_r<1 \), to fit the experiment, which
models the effect of scattering in the GNR channel. This is a simplified treatment of scattering but is expected to have a negligible effect on the extracted value of $E_g$, since thermionic emission over and tunnelling through barriers play a dominant role in the extraction process as described below.

The procedure to extract $E_g$ is described as follows. The minimum conductance for a given bandgap is found for each temperature point (in the range of 70K to 290K) by the self-consistent NEGF simulation. A root mean square (RMS) error is defined as

$$\sigma = \langle [\langle G(T) - G_{\text{exp}}(T) \rangle / G_{\text{exp}}(T) \rangle^2 \rangle^{1/2},$$

where $G(T)$ and $G_{\text{exp}}(T)$ are the simulated and experimental conductance values at $T$, respectively, and the average is taken over different temperatures. We found that the slope of the log($G$) vs. -1/$T$ curve is dominantly determined by the bandgap for negative SB height values, and it is independent of the exact value of $T_r$. After a group of curves of different bandgaps are simulated, the best fitting bandgap (i.e., the extracted bandgap) is given by the curve that has the smallest RMS error, $\sigma_{\text{min}}$.

For the three high quality GNR devices, the extracted bandgaps by assuming single-layer GNRs are $E_g=72$ meV, $E_g=60$ meV and $E_g=49$ meV for GNR1, 2 and 3 respectively. By allowing a fitting error of $2\sigma_{\text{min}}$, the extracted $E_g$ of the three devices can be varied by $\pm18$ meV, $\pm17$ meV, and $\pm15$ meV, respectively, from their best fitting values. If a twisted bilayer GNR is considered, the Hamiltonian of a twisted bilayer graphene can be simplified to an effective Dirac Hamiltonian similar to a single-layer based on the perturbation theory, but with a renormalized Fermi velocity, where the renormalization factor is about 0.8 [2]. By using a renormalization factor of 0.8, the extracted $E_g$ by the best fitting reduces by 10 meV and 5 meV for GNR1 and GNR2, respectively, which are within the error range indicated above.
**Figure S2.** Fitting the measured minimum conductance (blue solid lines) in log scale as a function of \(-1/T\) by the NEGF simulation (red dashed lines) for three high quality GNR devices. The temperature varies from 70K to 290K. The extracted bandgaps by the best fitting are \(E_g=72\) meV, \(E_g=60\) meV and \(E_g=49\) meV for GNR1, 2 and 3 as defined in the main text respectively.

3. Transport data of GNR1 \((L\sim 86\text{nm})\) at 4.2K in a different cool down.

**Figure S3.** Differential conductance as a function of \(V_{gs}\) and \(V_{ds}\) near the bandgap of GNR1 in the main text, taken in a separate cool down at 4.2 K. Only one central diamond appeared in the data. There were two gate switching events marked by the white arrows. The blue dashed lines were drawn as a guide to the eye for the big diamond (left) corresponding to the
bandgap and a small diamond (right).

4. **Phase coherent transport in GNR devices.**

We observed phase coherent transport in several GNR devices in the p-channel away from the bandgap region. Figure S3 showed two such examples taken on GNR1 and GNR2. Differential conductance as a function of bias voltage $V_{ds}$ and gate voltage $V_{gs}$ showed Fabry-Perot like interference [3]. As marked by the white arrows, the characteristic energy scale of GNR1 and GNR2 is $V_c\sim19$ mV and 10 meV, respectively, in good agreement with the calculated value of $V_c \approx \frac{h v_F^0}{2L\cdot e} \sim 21$ mV and 13 meV, where $v_F^0 \sim 8.7 \times 10^5$ m/s is the Fermi velocity of 2D graphene and $L$ is the channel length [3].

Figure S4. Differential conductance as a function of $V_{gs}$ and $V_{ds}$ in the hole channel away from the bandgap region, taken on (a) GNR1 and (b) GNR2, showing Fabry-Perot interference patterns. The white arrows point to the characteristic energy $V_c$ for both devices.

5. **Low temperature conductance of wider GNR devices.**
Figure S5. Zero bias differential conductance vs $V_{gs}$ for a $w\sim 52$ nm (a) and $w\sim 27$ nm (b) GNR devices at 4.2 K. At negative $V_{gs}$, they both exhibited higher conductance than $4e^2/h$, suggesting that more than two doubly degenerate subbands were involved in the transport. Wider GNRs tend to have more subbands involved probably due to the small subband spacings.

6. Calculation of the excited states energy and comparison with experiments.

Both single-layer and non-AB-stacked bilayer GNRs were examined. We used an atomistic $P_z$ orbital tight binding (TB) model with nearest neighbour interaction to compute the single-layer graphene $E$-$k$ [1]. The bandgap and excited states of single-layer GNRs were derived by quantizing the $E$-$k$ with particle-in-a-box boundary conditions, i.e. $k_{x,m}=m\pi/W$, and $k_{y,n}=n\pi/L$, where $k_x$ ($k_y$) is the wave vector along width (length) direction with regard to the $\Gamma$ point of the graphene Brillouin zone, $W(L)$ is the GNR width (length), and $m$ and $n$ are positive integers. The QD energy levels derived from the lowest semiconducting subband can be approximated by $E(k_x(n))=\pm\sqrt{(h\nu_x\pi/3W)^2+(h\nu_y n\pi/L)^2}$. For non-AB-stacked bilayer GNRs, we computed the bandgap and excited states by quantizing the wave vectors of non-AB-stacked bilayer graphene with Moiré patterns. The band structures of the non-AB-stacked bilayer graphene were computed using the TB parameters as described in Ref. [4]

Due to the uncertainties in the edge atomistic structures, number of layers, and layer stacking structure and simplicity of the calculation approach, the comparison to the experiment
is qualitative and only carries an order of magnitude meaning. We did calculations for single-layer GNRs and bilayer GNRs with different rotation angles of Moiré patterns. Note that the set of the rotation angles is infinite and therefore only a few representative calculations are listed in Table S1 for GNR1 and Table S2 for GNR2. In the low resolution scan as shown in Fig. 3f, we were able to assign all the observed excited states to the expected level spacings (Table S2). We note that in the scan as shown in Fig. 3f, not all the expected levels (such as $\Delta \varepsilon_{21}$) show up probably due to low resolution.

Table S1: Calculated bandgap and excited states for specific structures compared to the experiment data of GNR1

<table>
<thead>
<tr>
<th>Rotation angle of bilayer Moiré pattern</th>
<th>GNR Band gap (meV)</th>
<th>$\Delta \varepsilon_{21}$ (meV)</th>
<th>$\Delta \varepsilon_{31}$ (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>32.2</td>
<td>55.3</td>
<td>6.6</td>
<td>18.3</td>
</tr>
<tr>
<td>21.8</td>
<td>61.5</td>
<td>2.0</td>
<td>13.5</td>
</tr>
<tr>
<td>13.2</td>
<td>70.6</td>
<td>7.9</td>
<td>13.3</td>
</tr>
<tr>
<td>9.43</td>
<td>54.8</td>
<td>10.6</td>
<td>14.8</td>
</tr>
<tr>
<td>6.01</td>
<td>58.2</td>
<td>11.5</td>
<td>14.3</td>
</tr>
<tr>
<td>Single-layer GNR</td>
<td>84.9</td>
<td>12.2</td>
<td>28.3</td>
</tr>
<tr>
<td>Experiment</td>
<td>72±18</td>
<td>3.6</td>
<td>16.2</td>
</tr>
</tbody>
</table>

Table S2: Calculated bandgap and excited states for specific structures compared to the experiment data of GNR2

<table>
<thead>
<tr>
<th>Rotation angle of bilayer Moiré pattern</th>
<th>GNR Band gap (meV)</th>
<th>$\Delta \varepsilon_{21}$ (meV)</th>
<th>$\Delta \varepsilon_{31}$ (meV)</th>
<th>$\Delta \varepsilon_{41}$ (meV)</th>
<th>$\Delta \varepsilon_{32}$ (meV)</th>
<th>$\Delta \varepsilon_{42}$ (meV)</th>
<th>$\Delta \varepsilon_{43}$ (meV)</th>
<th>$\Delta \varepsilon_{53}$ (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>32.2</td>
<td>53.4</td>
<td>3.4</td>
<td>10.6</td>
<td>20.2</td>
<td>7.2</td>
<td>16.8</td>
<td>9.5</td>
<td>20.3</td>
</tr>
<tr>
<td>21.8</td>
<td>64.6</td>
<td>4.6</td>
<td>8.4</td>
<td>13.2</td>
<td>3.8</td>
<td>8.6</td>
<td>4.8</td>
<td>11.1</td>
</tr>
<tr>
<td>13.2</td>
<td>57.1</td>
<td>3.3</td>
<td>9.8</td>
<td>18.5</td>
<td>6.5</td>
<td>15.2</td>
<td>8.7</td>
<td>18.6</td>
</tr>
<tr>
<td>9.43</td>
<td>54.9</td>
<td>2.8</td>
<td>7.9</td>
<td>15.7</td>
<td>5.4</td>
<td>12.9</td>
<td>7.5</td>
<td>16.2</td>
</tr>
<tr>
<td>6.01</td>
<td>53.8</td>
<td>4.5</td>
<td>11.4</td>
<td>19.6</td>
<td>6.9</td>
<td>15.1</td>
<td>8.2</td>
<td>17.2</td>
</tr>
<tr>
<td>Single-layer GNR</td>
<td>70.1</td>
<td>6.1</td>
<td>14.7</td>
<td>24.8</td>
<td>8.6</td>
<td>18.7</td>
<td>10.1</td>
<td>18.9</td>
</tr>
<tr>
<td>Experiment (from excited)</td>
<td>60±17</td>
<td>2.5-3.6</td>
<td>8.2-10.1</td>
<td>19.2-19.8</td>
<td>5.3-6.2</td>
<td>11.5-16.3</td>
<td>9.6-12.5</td>
<td>19.7</td>
</tr>
</tbody>
</table>
7. Simulation of Coulomb blockade pattern of GNR2 and comparison with experiments.

A single-electron charging simulator is developed based on the many-particle Fock space master equation [1]. The coupling of the QD to the source and drain causes the transition of the QD state from one many-body state to another, which can result in the source-drain current. The input parameters of the simulator are the single particle energy levels, coupling capacitances, and source/drain contact broadening. The output is the conductance (or current) as a function of the applied voltages. At a low temperature ($T<5\ K$) and small magnitude of gate biases, the condition to use the master equation, $U_0\gg k_BT$ and $\Gamma$, is satisfied, where $U_0$ is the single electron charging energy, and $\Gamma$ is the total broadening by the electrodes. The simulation captures Coulomb diamond shapes and sizes, as well as the excited state lines. By comparing the simulation results with experiments, one can clearly identify where each excited state line comes from as labelled in Fig. 3e. These excited state lines can stem from adjacent energy levels (e.g. $\varepsilon_2-\varepsilon_1$) as well as non-adjacent energy levels (e.g. $\varepsilon_3-\varepsilon_1$). One can also extract capacitances and single particle levels by the best fitting of the simulated results to the experimental measurements.

For GNR2, the gate capacitance is estimated as $C_g\sim0.87\ aF$ from the gate voltage periods of the conductance peaks at low $V_{ds}$. The drain capacitance $C_d\sim2.13\ aF$ is found through the slope of the Coulomb diamond boundaries of the negative slope sides. From the single electron charging energy, the total capacitance of the QD can be computed, and the source capacitance of $C_s\sim2.70\ aF$ is obtained. From the experimental data in Fig. 3d and simulated CB pattern in Fig.3e (with $C_g=0.87\ aF$, $C_s=2.70\ aF$ $C_d=2.13\ aF$, and a source/drain broadening of 0.05 meV), we can obtain the following energy spacing values, $\Delta\varepsilon_{41}\sim19.4$ or 19.8 meV, $\Delta\varepsilon_{31}\sim10.1$ meV and $\Delta\varepsilon_{21}\sim2.5$ or 3.6 meV.
8. Electron transport data of a lithographic GNR.

In comparison with high quality GNR devices from unzipping MWNTs, we lithographically patterned GNR devices from pristine single-layer exfoliated graphene with similar dimensions. At low temperatures, the lithographic GNRs typically showed defect dominant behavior distinct from our high quality GNRs. Fig. S5 presents the transport data of a representative lithographic GNR device.

Different from the high quality GNRs, lithographic GNR devices usually showed lower conductivity and mobility as shown in Fig. S5a ($\sigma_{on} \sim 0.19 \text{mS}, \mu \sim 210 \text{cm}^2/\text{Vs}$). The on state conductance upon cooling was constant down to $T^* \sim 100 \text{K}$, followed by rapid decrease at lower temperature (Fig. S5a, inset). Near the Dirac point, the lithographic GNR showed suppressed conductance over a relatively wide region in the $G-V_{gs}$ characteristics at low temperature ($\Delta V_{gs} \sim 10 \text{V}$, ~10 times that of GNR1), with some resonances inside (Fig. S5b). Similar behavior has been observed in lithographic GNRs and graphene nanoconstrictions and attributed to transport gap resulting from edge disorders or charged impurities [5-9].

Theoretical calculations have shown that the density of states of GNRs with edge disorders are dominated by localized states near the Dirac point, and the charge transport could be through variable range hopping between these localized states at low temperature [10-12]. The sharp resonances in the transport gap are signatures of resonant tunneling through the localized states [5]. We note that the resonances in the transport gap only start to become obvious below the same $T^* \sim 100 \text{K}$ (Fig. S5b). This is expected because when $T<T^*$, the charge carriers tend to localize near the defects in the aforementioned transport gap picture [5, 10], leading to the decrease in conductance. $k_B T^* \sim 8 \text{meV}$ is also in good agreement with the characteristic temperature $T^*$ in Ref. 6. When $T>T^*$, $G_{min}$ appeared to follow a thermally activated behavior [5]. At 4.2 K, the transport features near the Dirac point were also highly different from the high quality GNRs (Fig. S5c). Over ~30 V span in $V_{gs}$ (the transport gap), the transport features were dominated by CB diamonds with sizes ranging from ~10 meV to ~30 meV. Some of the diamonds were not closed indicating multiple QD behavior [6, 7]. These features were similar to previously reported short channel lithographic GNRs [6-9]. In this case, the transport gap was dominant due to large numbers of localized states most likely
by edge defects [6-12]. Coulomb diamonds did not close due to multiple dots in series as a result of defects along the GNR [6, 7]. Excited states were rarely observed in lithographically derived GNR QDs.

**Figure S6.** Transport measurement of a representative lithographic GNR device (L~75 nm). (a) Room temperature low bias ($V_{ds}=1$ mV) $G$-$V_{gs}$ characteristics of the lithographic GNR device. Lower inset is AFM images of the devices. Upper inset shows $G$ vs. $T$ at $V_{gs}$ = $V_{Dirac}$ - 40 V in the p-channel. (b) Low bias ($V_{ds}=1$ mV) $G$-$V_{gs}$ characteristics of the lithographic GNR device at various temperatures down to 50 K. (c) Differential conductance of the lithographic GNR as a function of $V_{gs}$ and $V_{ds}$ in the transport gap at 4.2 K. In the transport gap, CB diamonds with size ranging from ~10 meV to ~30 meV are observed over ~30 V $V_{gs}$ span.

9. **Additional electron transport data of unzipping derived GNRs.**

Fig. S6 and S7 show electron transport data of two lower quality unzipping derived GNRs with $L$~175nm. The p-channel conductance was lower than $\sim 2e^2/h$ for both...
devices at room temperature and decreased at lower temperatures, similar to lithographic GNRs. We measured the gap region near the Dirac point at $T=4.2$ K, and observed many small diamonds (some of them were irregular without complete closure) over a large $V_{gs}$ range, indicating the deviation from a single quantum dot behaviour likely due to defects on the ribbon.

Note that we have also measured some wider GNRs with $w\sim 20\text{-}30$ nm. Down to the base temperature of our cryostat (~2 K), the conductance of these GNRs near the Dirac point was usually not depleted without Coulomb blockade likely due to the more metallic nature of these wider GNRs. This was also reflected from the weaker $G_{\text{min}}$ (conductance at the Dirac point) vs. $-1/T$ dependence than that of narrower ribbons in Fig.S1.

Figure S7. Electron transport data of a $w\sim 17 \text{nm}, L\sim 330 \text{nm}$ unzipping derived GNR device. (a) Low bias ($V_{ds}=1$ mV) $G$-$V_{gs}$ characteristics of the GNR device under various temperatures
Figure S8. Electron transport data of a \( w \sim 12 \) nm, \( L \sim 175 \) nm unzipping derived GNR device. (a) Low bias \( (V_{ds}=1 \) mV) \( G-V_{gs} \) characteristics of the GNR device under various temperatures down to 50 K. Inset shows the AFM image of the device. (b) Zero bias differential conductance as a function of \( V_{gs} \) of the GNR device at 4.2 K. (c) Top panel: differential conductance as a function of \( V_{gs} \) and \( V_{ds} \) of the GNR device near the Dirac point, showing many small diamonds without a clean, large diamond corresponding to the bandgap. Bottom panel: zero \( V_{ds} \) line cut from the top panel.
10. Raw data in Figure 3 of the main text without the dashed lines.

Figure S9. Differential conductance scans for GNR2 at 3.3 K without dashed lines. The data are the same as Fig. 3d and f in the main text.

11. Conductance plateaus of GNR1 and GNR2 at low temperatures.

We have observed possible signatures of multiple 1D subbands as conductance plateaus [13, 14] in several GNRs including GNR1 and GNR2 below ~100 K. The conductance plateaus were most clear at ~50-60 K, below which Fabry-Perot like oscillations started to kick in. Fig. S10 are $G$ vs $V_{gs}$ curves for GNR1 and GNR2 discussed in the manuscript. The conductance steps were ~0.9-1 $e^2/h$ for both cases, which was much greater than previously observed step sizes in GNRs [13, 14]. Due to the two-fold degeneracy of subbands in GNRs, these data suggest that the transmission coefficient at each contact is ~0.7, partly due to reflection at the contacts, and up to 4 subbands are involved in the transport of GNR1 and GNR2. We note that transport through multiple subbands was rarely observed in carbon nanotubes. For wider ribbons, more subbands were populated based on the high conductance.
(up to ~7 $e^2/h$) (Fig. S5), likely due to lower Schottky barriers to higher subbands.

Figure S10. $G$ vs $V_{gs}$ curves for GNR1 at 50 K (a) and GNR2 at 60 K (b). Conductance plateaus were observed in both cases with steps of ~0.9-1 $e^2/h$.

Reference: