Supporting Online Material for

Chemically Derived, Ultrasmooth Graphene Nanoribbon Semiconductors

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Chemically Derived, Ultra-Smooth Graphene Nano-Ribbon Semiconductors

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(1) Method of graphene nanoribbon (GNR) making.

Our GNR making method started by exfoliating expandable graphite (160-50N of Grafguard Inc., made by intercalating ~350 micron scale graphite flakes with sulfuric acid and nitric acid) at 1000°C in forming gas for 1 min, sonicating the resulting exfoliated material in a 1,2-dichloroethane (DCE) solution of poly(m-phenylenevinylene-co-2,5-dioctoxy-p-phenylenevinylene) (PmPV) (0.1mg/mL) to disperse and break up the graphenes into small graphene sheets and GNRs, and
centrifuging the suspension to retain the GNRs (together with small sheets) in the supernatant and remove other materials including large graphene pieces and not fully exfoliated graphite flakes. Note that only ~ 0.5% of the starting material was retained in the supernatant, which suggests that the majority of the material remained in many layer structures that were heavy and removed by centrifugation. The retained graphene in the suspension were comprised of lighter single and few-layer graphene in ribbon and sheet forms. The number of ribbons was sufficient for depositing onto substrates for characterizations by microscopy and electrical transport experiments. The high temperature exfoliation step was a crucial step to the preparation of graphene nanoribbons. It resulted in many thin graphite sheets including a small percentage of single and few-layer graphene. This was indicated by that after exfoliation, the volume of the exfoliated graphite (Fig. S1B) was hundreds of times higher than before exfoliation (Fig. S1A). The BET surface area of such exfoliated graphite was on the order of ~60m²/g (1), much higher than before exfoliation but still far below that of single-layer graphene. Thus, much room still exists to better exfoliate graphite and increase the yield of single and few-layers by chemical methods.

The use of PmPV and DCE were also key to the preparation of GNR suspension, similar to suspending carbon nanotubes (2, 3). We tried various other solvents and coating molecules and the combination of PmPV/DCE was the best for suspending graphene. The suspensions were made as follows: The exfoliated graphite (~1mg) was bath-sonicated with PmPV (~1mg) in 10mL DCE for 30mins to form a uniform dispersion (Fig. S1C). The suspension was then centrifuged at 15k rpm (round per

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minute) for 5mins to remove the big pieces and aggregates. The supernatant (Fig. S1D) contained mostly graphene nanoribbons and small pieces of graphene sheets well solubilized in DCE with adsorbed PmPV molecules (Fig. S1E). The supernatant was collected and stored for characterizations and making GNR devices.

Figure S1. Schematic process of making suspensions containing graphene nanoribbons. (A) A photograph of expandable graphite flakes. (B) A photograph of thermally exfoliated graphite. Notice the dramatic volume increase after exfoliation. XPS showed little oxygen content (similar to pristine graphite flakes) in the exfoliated graphite after this high temperature treatment step. (C) A photograph of the uniform suspension obtained after 30mins sonication of the exfoliated graphite in a PmPV/DCE solution. (D) Photograph of the supernatant collected after centrifuge. (E) Schematic drawing of a graphene nanoribbon with two units of a PmPV chain adsorbed on the graphene ribbon.

(2) Elemental analysis and spectroscopic analysis.

We shipped our exfoliated graphite (step B in Fig. S1) to Atlantic Microlab, Inc. for elemental (CHONS) analysis. CHNS elements were analyzed by combustion using automatic analyzers. Oxygen content analysis was performed by pyrolysis. The measurements used ~ 10 mg material. The sample was dried under vacuum. Results
showed that the exfoliated graphite contained 95.7% C, 0.31% of O, 0.86% S, and the HN elements were below the detection limit of 0.3%. The remaining uncounted few percent of materials were attributed to impurities most likely existed in the original expandable graphite. Currently, we do not have ~10mg of ribbon samples (step D in Fig.S1) for similar analysis.

We carried out X-ray photoelectron spectroscopy (XPS) analysis of our ribbon sample. Sample preparation involved depositing materials from step D of Fig.S1 onto a silicon substrate by repeated drop-drying. The large amount of deposits was then analyzed by XPS (SSI S-Probe Monochromatized XPS Spectrometer, which uses Al (Kα) radiation as a probe. Analysis spot size is 150 micron by 800 micron.). For comparison, we also took XPS spectra of a pristine highly oriented pyrolytic graphite HOPG sample. Fig.S2 shows that the C1s peak structure of our ribbon sample was similar to that of pristine HOPG, without significant signals corresponding to C-O species. This suggests the high pristine nature of our ribbon samples without excessive covalent chemical functionalization as in the case of graphite oxide (4). For graphite oxide known to be heavily functionalized covalently, high signals in the higher binding energy region corresponding to C-O bonding was observed in XPS (4), in strong contrast to our ribbon samples and pristine HOPG.

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Figure S2. The C1s XPS spectra recorded with our graphene nanoribbon deposits on a substrate and vacuum annealed at 600 °C (black curve) and a pristine HOPG crystal (red curve) respectively.

(3) Characterization of graphene ribbon width and thickness (number of layers) by AFM.

Care was taken to measure the ribbon width accurately using AFM since the radius of our Si AFM tips (Veeco multi75) was around 10-20nm. To count for the tip size effect, we used diameter-separated Hipco SWNT samples with very narrow diameter distribution around 1.1nm to calibrate the AFM tip. We took high quality images of the SWNTs and measured the apparent widths to glean tip width (typically ~ 6-7nm), which was then corrected from the apparent width of GNRs measured by AFM. From > 100 ribbons we imaged in this work, we often observed a few discrete heights, namely 1.1nm, 1.5nm, 1.9nm, and never observed a GNR or other shaped graphene with height less than 1nm. Thicker ribbons were also observed but not used for further studies such as transport measurements. We assigned the GNRs with height ~1.1nm, ~1.5nm, and ~1.9nm to be 1, 2, 3-layer GNRs, respectively. This assignment was also consistent with
the reported AFM results on few-layer graphene sheets, where the single layer graphene is always ~1nm (5, 6), possibly due to different attraction force between AFM tips and graphene as compared to SiO\textsubscript{2} and non-perfect interface between graphene and SiO\textsubscript{2}. Below we presented the raw height profile data (Fig. S3) for several 1-layer, 2-layer and 3-layer ribbons in Fig. 1 and Fig. 2 of the main text.

Figure S3. Topographic height profiles of several ribbons in Fig. 1 and Fig. 2 of main text. In each row, the left image is the same as shown in Fig. 1 or Fig. 2 of the main text. The middle image is a zoom-in image, with which topographic analysis is done. (A), (B), and (C) are left panel of Fig. 1B, right panel of Fig. 1D, and Fig. 2B of the main text respectively. They are single layer graphene with the height of about ~1.0nm. (D), (E), and (F) are middle panel of Fig. 1B, left panel of Fig. 1F, and Fig. 2A of the main text respectively. These are two-layer GNRs with the height of ~1.5nm. (G), (H), and (I) are left panel of Fig. 1C, middle panel of Fig. 1D, and Fig. 2D of the main text respectively. These are three-layer graphene with the height of ~1.9nm.

We imaged our GNRs by using single-walled carbon nanotube AFM tips (7). Such tips were comprised of a single or small bundle of nanotubes (2-5nm in diameter) and gave higher lateral resolution than conventional Si tips. Indeed, we observed that AFM with nanotube tips gave narrower apparent width than conventional tips by ~4nm. Fig.S4 shows an example of a sub-10nm GNR exhibiting apparent width of 12nm and

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8nm imaged by Si tip and nanotube tip respectively. The nanotube tips still have a finite size, which will need to be taken into account in order to measure the widths of GNRs.
Figure S4. (A) An AFM image of a sub-10nm GNR imaged by a Si tip, (B) AFM image of the same ribbon imaged by a carbon nanotube tip. (C) & (D) Topographic line-cut measurements for the two images in (A) and (B), showing an apparent width of the ribbon of ~12nm (Si tip) and ~8nm (nanotube tip) respectively.

Optical microscopy has been used to determine the thickness and layer number of large graphene sheets in the literature. The narrow GNRs in the current work were difficult to resolve and identify under a typical optical microscope. Raman spectra have been well used before to determine the number of layers of big graphene sheets. However, the Raman spectroscopic properties of GNRs with narrow widths are not known and require systematic investigation by experiments and theory (8). The Raman spectra of GNRs may differ significantly from large graphene with new features due to quantum confinement of phonon and electron (6). Systematic Raman spectroscopic investigation of our GNRs is ongoing.

(4) Making Graphene nanoribbon FETs.

GNRs were deposited onto 300nm SiO₂/p⁺⁺ Si substrate with arrays of pre-

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deposited metal markers (2nm Ti/20nm Au) by soaking the substrate in the graphene suspension in PmPV/DCE solution for 20min, rinsing with isopropanol and blow-dry with argon. The chip was calcined in air at 400°C to burn away PmPV on the GNRs and annealed in vacuum at 600°C to further clean the surface. Tapping mode AFM was then used to locate ribbons and record relative locations to the pre-fabricated markers. S/D electrode pattern was then designed for electrically contacting the GNRs, which was carried out by electron beam lithography, 20nm Pd metal deposition and liftoff. The devices were then annealed in 1000 sccm argon at 220°C for 15 min to improve contact quality. We took the AFM image of GNRs in our devices immediately after annealing to avoid contamination of graphene due to absorption of various molecules. After AFM, we carried out electrical characterizations of our devices using a semiconductor analyzer (Agilent 4156C, sensitivity ~10fA) to record transfer $I_{ds}$ vs. $V_{gs}$ and $I_{ds}-V_{ds}$ curves for the graphene devices.

(5) Comparison with theoretical results of graphene nano-ribbon bandgap $E_g$ versus width $w$.

In Fig. 4B of main text, we plot first-principles based results of $E_g$ versus $w$ from Ref. 7. Blue, orange and purple lines denote arm-chair edged GNRs with dimer lines $N_a=3p$, $3p+1$ and $3p+2$ ($p$ is integer) across the ribbons respectively. The ribbon width is

$$w = \frac{\sqrt{3}(N_a-1)}{2} \times a_{c-c},$$

where $a_{c-c} \sim 0.142$nm is carbon-carbon bond length. The bandgaps are

$$E_{g,3p} = \Delta_{3p}^0 - \frac{8\delta\ell}{3p + 1} \sin^2 \frac{p\pi}{3p + 1}$$

(1)

$$E_{g,3p+1} = \Delta_{3p+1}^0 + \frac{8\delta\ell}{3p + 2} \sin^2 \frac{(p+1)\pi}{3p + 2}$$

(2)
\[ E_{g,3p+2} = \Delta_{3p+2}^0 - \frac{2|\delta|}{p+1} \]  

(3)

where \[ \Delta_{3p}^0 = t\left(4\cos\frac{p\pi}{3p+1} - 2\right), \Delta_{3p+1}^0 = t\left(2 - 4\cos\frac{(p+1)\pi}{3p+2}\right), \Delta_{3p+2}^0 = 0, t=2.7\text{eV and} \]

\[ \delta = 0.12. \]

The green line in Fig. 4b denotes calculate bandgaps for zig-zag edged GNRs, for which the equation is

\[ E_{g}^{\text{zigzag}} (eV) = \frac{9.33}{w(\text{Å}) + 15}. \]  

(4)

(6) Transmission electron microscopy (TEM) characterization

We characterized our solution phase derived graphene by a Philips CM20 transmission electron microscope (TEM) at an accelerating voltage of 200kV. The TEM samples were prepared by drying a droplet of the graphene suspensions on a lacey carbon grid. We observed many ribbon structures in the TEM with various widths and lengths. Fig.S5 below shows a GNR with varying widths from about ~20nm to ~10nm along the ribbon length (Fig.S5A). We recorded electron diffraction (ED) patterns of graphene over many areas on the TEM grid and clearly observed hexagonal diffraction patterns corresponding to graphene (Fig. S5C). Note that no carbon nanotubes were observed through our TEM studies of graphene materials in our suspensions.
Figure S5. TEM and electron diffraction studies of graphene nanoribbon samples. (A) A TEM image showing a graphene nano-ribbon (~1 micron long) with width changing from about ~20nm to slightly below 10nm. (B) A zoom-in view of the ribbon in the marked region of (A). Notice the very smooth edges of the GNR. (C) A typical electron diffraction pattern of recorder for the graphene sample.

(7) Raman spectroscopic characterization of graphene samples

We used surface enhanced Raman to characterize graphene materials deposited on Au coated substrates, using a Renishaw micro-Raman instrument with an excitation laser wavelength of 785 nm and a laser spot size of about 2 microns. Samples for Raman measurements were prepared by drying droplets of the graphene ribbon suspension onto
a piece of glass substrate coated with 0.5nm Ti and 5nm gold. We carried out Raman spectroscopic mapping after annealing the substrate in H₂ for 3min to aggregate the gold film into gold particles. This was a procedure found to give drastic surface enhanced Raman signals to Hipco single-walled carbon nanotubes (SWNT) in control experiments (Fig.S6D and S6E), even for low density SWNTs deposited onto the substrate without drying the SWNT suspension droplet. For SWNT control sample, Raman mapping was done in the 1350-1840cm⁻¹ (G peak range) and 160-300cm⁻¹ (SWNT radial breathing mode or RBM region). We readily observed strong RBM signals of SWNTs in control Hipco nanotube sample (Fig.S6D and 6E). For graphene nanoribbon samples, we observed the graphene G peaks over the sample (Fig. S6A) but never observed any RBM peaks (Fig. S6B and S6C) over large areas of the sample. In fact, Raman mapping results over the graphene sample in the 160-300cm⁻¹ region were identical to those on blank substrates (Fig. S6F and S6G) without any deposited graphene, without any RBM modes observed. This confirmed that our graphene suspension did not contain any SWNTs, and the sub-10nm GNRs in the suspension were not SWNTs caused by any sample contaminations.
Figure S6. Surface enhanced Raman mapping of graphene nanoribbons and control samples. (A) A Raman spectrum recorded on a substrate with deposited graphene in the G-band 1350-1840 cm\textsuperscript{-1} region. (B) A ~60 μm\textsuperscript{2} Raman map recorded on a substrate with deposited graphene in the 100-300 cm\textsuperscript{-1} region. (C) A typical Raman spectrum from (B). (D) A ~60 μm\textsuperscript{2} Raman map of a control sample with deposited Hipco SWNTs in the 100-300 cm\textsuperscript{-1} region. (E) A typical Raman spectrum from (D). (F) A ~60 μm\textsuperscript{2} Raman map recorded on a control sample, i.e., a blank substrate in the 100-300 cm\textsuperscript{-1} region. (G) A typical Raman spectrum from (F).

(8) Electrical transport properties of GNRs wider than 10nm

Figure S7 below shows typical electrical characteristics of GNR devices with ribbon widths of w \textasciitilde 20 and 50nm respectively. We observed that at room temperature, the $I_{on}/I_{off}$ ratio was less than 10 for the 18nm wide ribbon, and less than 2 for the 48nm wide ribbon (defined as $I_{ds}(V_{gs} = -20V)/I_{ds}(V_{gs} = 40V)$).

Note that electrical transport measurements carried out at various temperatures further revealed the high quality pristine nature of our GNRs. Specifically, the high quality of our GNRs was evident from phase coherent Fabry-Perot type of conductance interference for w \textasciitilde 30 to 50nm ribbons at low temperatures (data not shown), similar to those observed in high quality carbon nanotubes. This further confirmed the lack of extensive chemical functionalization of the GNRs obtained by the method presented here. It is worth mentioning that similar degree of sonication in the same solvent DCE has been used previously for SWNTs used in electrical transport measurements, with phase coherent transport routinely observed (9, 10), indicating no extensive covalent defects are introduced on the sub-micron length scale by the procedure.


Figure S7. Electrical properties of widths $w>10$ nm graphene nanoribbons. (A) $I_{ds}$ versus $V_{ds}$ curves for a ~48 nm wide GNR device under different gate voltages. From bottom to top, $V_{gs}$ is from -20 V to 30 V at 10 V/step. Inset is the transfer characteristics of this device at $V_{ds} = -10$ mV. The picture on the right is the AFM image of this device, with a 100 nm scale bar. The thickness of this device is ~1.6 nm (2-layer). (B) $I_{ds}$ versus $V_{ds}$ curves for a 18 nm wide GNR device under different gate voltages. From bottom to top, $V_{gs}$ is from -20 V to 50 V at 10 V/step. Inset is the transfer characteristics of this device at $V_{ds} = -10$ mV. The thickness of this device is ~1.5 nm (2-layer). The picture on the right is the AFM image of this device, with a 100 nm scale bar. Roughness in the image was caused by residue photoresist used in device fabrication. The GNR exhibit very smooth edges in images recorded before device fabrication (data not shown). (C) Topographic height profile of the ~48 nm wide GNR in (A). Note that the surface roughness of 300 nm SiO$_2$ substrate used in this work was <~0.4 nm measured by AFM over 2 $\mu$m x 2 $\mu$m areas of the substrate.