

Large-Scale Solution Synthesis of Narrow Graphene Nanoribbons

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According to theoretical studies, narrow graphene nanoribbons (GNRs) with atomically precise armchair edges and widths less than 2 nm have a bandgap comparable to that in silicon (1.1 eV), which makes them potentially promising for logic applications. Different top-down fabrication approaches typically yield ribbons with width > 10 nm and have limited control over their edge structure. Here we demonstrate a novel bottom-up approach that yields gram quantities of high-aspect-ratio GNRs, which are only ~ 1 nm wide and have atomically smooth armchair edges. These ribbons are shown to have a large electronic bandgap of about 1.3 eV, which is significantly higher than any value reported so far in experimental studies of GNRs prepared by top-down approaches. These synthetic GNRs could have lengths over 100 nm and self-assemble in highly-ordered few-micrometer-long “nanobelts” that can be visualized by conventional microscopy techniques, and potentially used for fabrication of electronic devices and circuits.

Because of its extraordinary electronic, mechanical, thermal and optical properties, graphene is often considered as a complement, and in some cases even replacement for silicon in future electronics.¹⁻³ However, the absence of the energy bandgap in graphene prevents its use in logic applications.^{2,3} According to theoretical studies, a bandgap comparable to that in silicon (1.1 eV) could be found in narrow graphene nanoribbons (GNRs) that have atomically precise armchair edges and widths less than 2 nm.^{4,5} Different top-down fabrication approaches, such as nanofabrication,^{6,7} sonochemical method,⁸ nanowire lithography,^{9,10} nanoscale cutting of graphene using nickel nanoparticles^{11,12} or a diamond knife,¹³ and unzipping of carbon nanotubes,¹⁴⁻¹⁹ typically yield ribbons with width > 10 nm and have limited control over their edge structure. Although it was demonstrated by several groups that such GNRs could exhibit an insulating state in electrical measurements, it was later argued that the observed transport bandgaps of up to ~200-400 meV⁷⁻⁹ are likely to be caused by strong localization effects due to edge disorder, rather than a true gap between valence and conduction bands.²⁰⁻²² Thus, it is important to develop techniques to produce large quantities of GNRs that are only 1-2 nm wide and have atomically precise armchair edges.

Large quantities of GNRs could be prepared by chemical vapor deposition, but the widths of such ribbons (20-300 nm) are too large to open a substantial electronic bandgap.²³ Narrow sulfur-terminated GNRs have been synthesized by decomposition of fullerenes or other molecular precursors inside carbon nanotubes,^{24,25} but the large-scale production of such ribbons, their separation from the host tubes and subsequent use for electronic devices are very challenging. Recently, Cai *et al.* have demonstrated that bottom-up chemical approaches have a great potential for synthesis of narrow GNRs.²⁶ Ribbons that are only a few benzene rings wide and have atomically smooth armchair edges were synthesized on a surface of either Au(111) or

Ag(111) single crystal by coupling molecular precursors into linear polyphenylenes followed by cyclodehydrogenation. This work demonstrates that bottom-up techniques could yield narrow atomically-engineered GNRs that are currently unachievable by any top-down approach, stimulating their detailed characterization,²⁷⁻³⁴ as well as further research and development of new synthetic methods for GNRs.

Of particular interest are novel solution-based approaches, which, in contrast to surface-limited coupling techniques, could yield bulk quantities of GNRs for large-scale applications.³⁵⁻⁴⁰ Also, GNRs prepared on a conductive Au (111) or Ag (111) single crystal cannot be directly used for device fabrication and electrical testing, and thus should be somehow transferred to a dielectric substrate, while GNR synthesized in solution could be conveniently deposited on any substrate of choice, such as Si/SiO₂. Here we report a solution-based synthetic approach for large quantities of GNRs that are ~ 1 nm wide, could have length > 100 nm and self-assemble in highly-ordered micrometer-long superstructures. These GNRs and especially their assemblies are long enough to bridge nanogaps fabricated by the standard electron-beam lithography.^{41, 42}

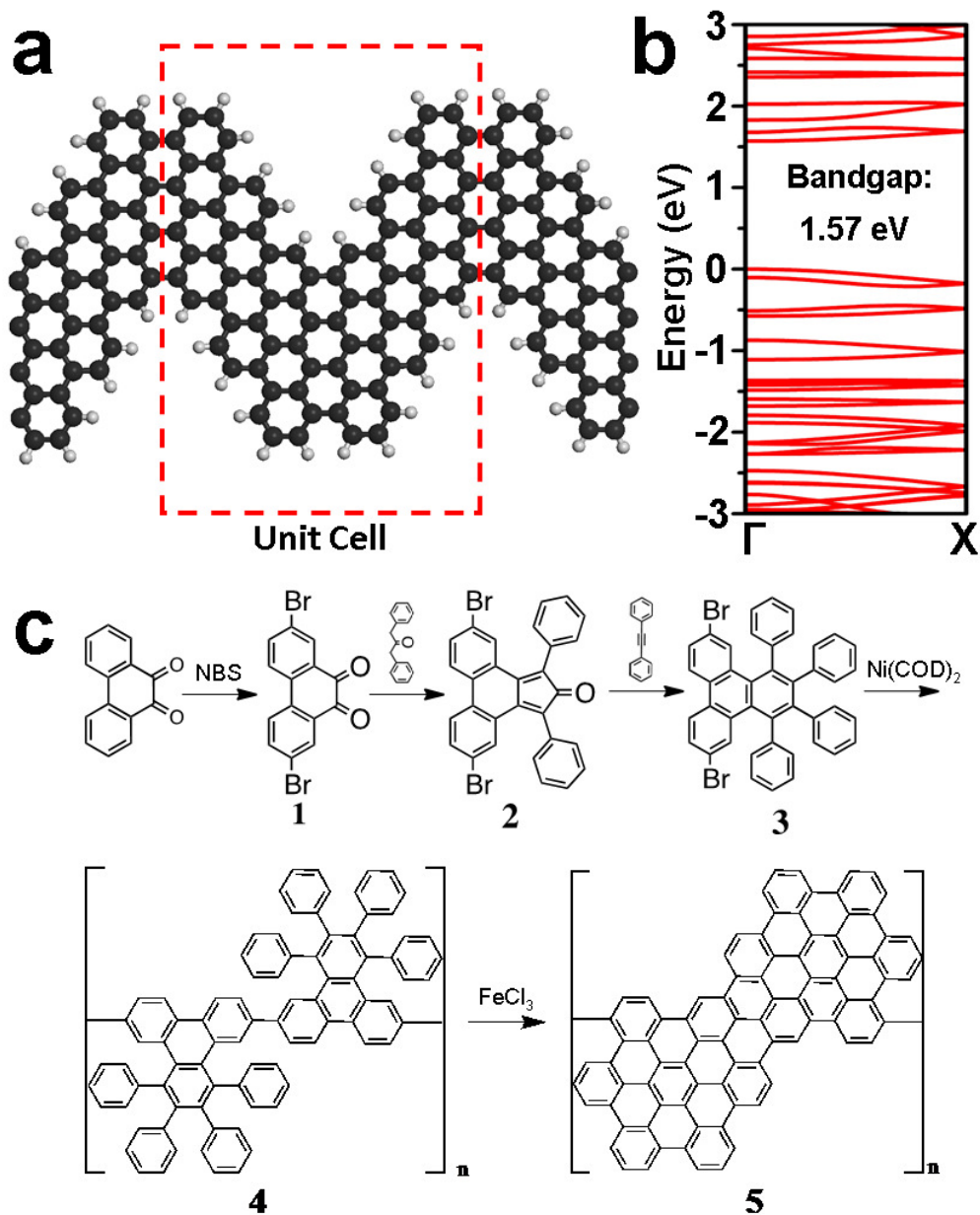


Figure 1. Synthesis of GNRs with a large electronic bandgap. (a) Schematic of the GNR synthesized in this study, and (b) the corresponding band structure calculated by the DFT method. (c) Reaction scheme used in this work, see text for details.

A particular GNR that we attempted to fabricate in this work is shown in Figure 1a; it has a width of only about 1 nm and uniform armchair edges. According to the density functional

theory (DFT) calculations (Figure 1b), this ribbon has an electronic bandgap of about ~ 1.6 eV (an even larger value would be obtained using an alternative computational approach^{27, 43}). This value is larger than that in silicon (1.1 eV), suggesting that such GNRs could be utilized for the fabrication of field-effect transistors (FETs) with high on-off ratios, and possibly even logic gates. Furthermore, a recent theoretical study suggests that these ribbons (Figure 1a) are a very promising material for optoelectronic applications,⁴⁴ that will require large quantities of such GNRs.

The reaction scheme used in this work to synthesize these GNRs is shown in Figure 1c. Briefly, it is based on a polymerization of pre-synthesized molecular precursors by a Ni⁰-mediated Yamamoto coupling⁴⁵ followed by a cyclodehydrogenation via a Scholl reaction using iron (III) chloride⁴⁶ to form GNRs. This synthetic approach is described in the Methods section with more details given in Supplementary Information (SI). We demonstrate that the procedure is scalable, and over 1 g of ribbons could be synthesized in a single synthesis; see SI. We believe that this approach is very general, and by using other molecular precursors instead of **3** it would be possible to synthesize other GNRs with different widths and geometries.²⁶

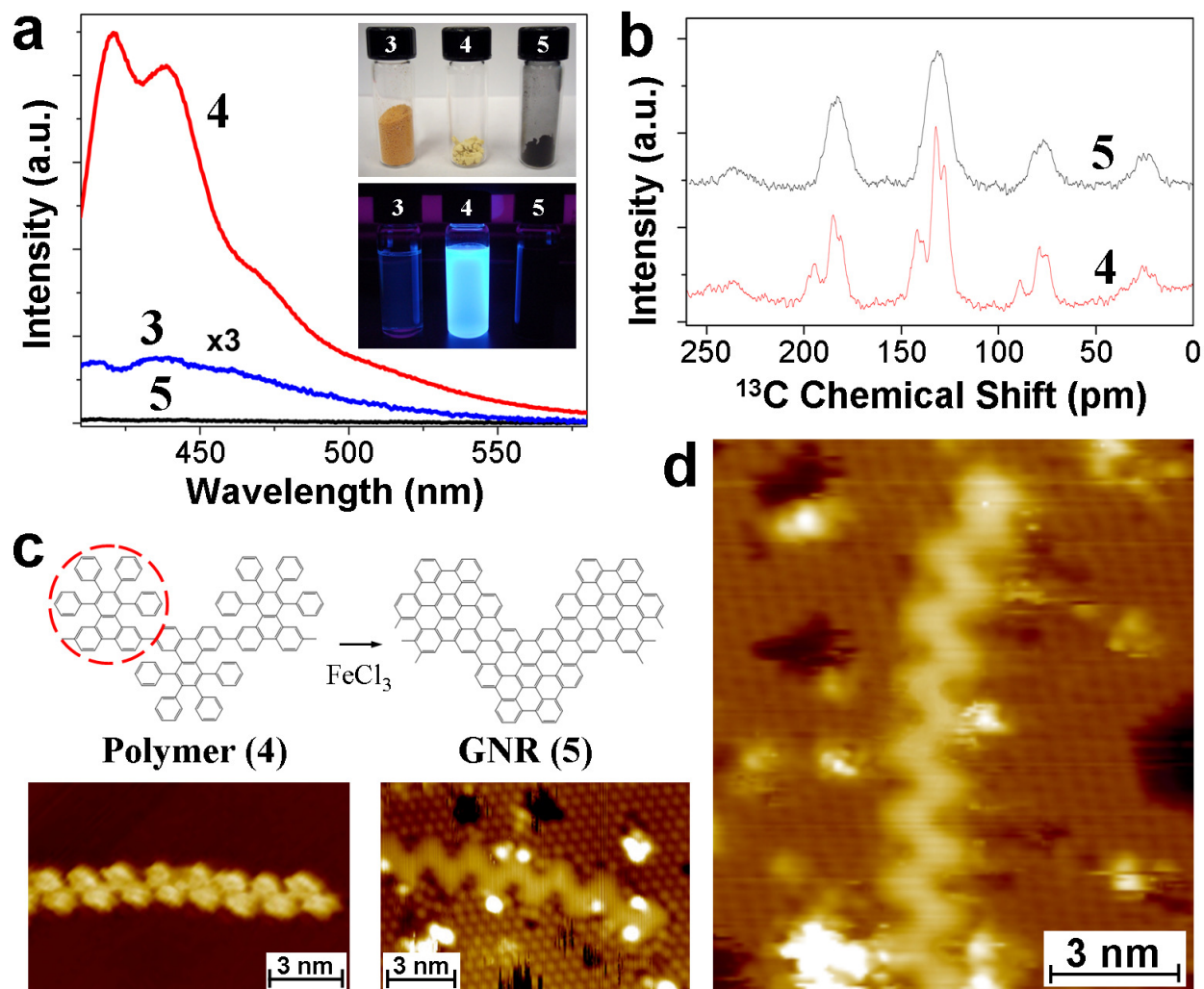


Figure 2. Comparison of GNRs and intermediate reaction products. (a) Photoluminescence spectra of the molecule **3**, polymer **4** and GNRs **5**; spectrum **3** is magnified by factor 3 for clarity. The top inset shows 5 ml vials with all three products; the bottom inset shows 5 ml vials with 0.167 mg/ml dispersions of the same products in dichloromethane, irradiated from the back by a 365 nm UV lamp; numbers on the vials correspond to the numbers in Figure 1c. (b) ¹³C NMR spectra for the polymer **4** and GNRs **5**. (c) Atomic structures and corresponding STM images of a polymer **4** and a GNR **5** deposited on a Au (111) single crystal. (d) STM image of another GNR **5** on Au (111).

Molecules **1-3** were characterized by mass spectrometry (MS) and/or ^{13}C nuclear magnetic resonance (NMR); see SI for details. Here we discuss the last two steps in the reaction scheme, i.e. transformations of molecule **3** to polymer **4** to GNR **5**. First of all, these products have different colors, as shown in the top inset in Figure 2a (see SI for comments regarding the color of **3**). Furthermore, this figure clearly shows that macroscopic quantities of all products, including GNRs, are attainable by the described synthetic approach. All three materials exhibit very different photoluminescence properties. The bottom inset in Figure 2a shows three vials with products **3**, **4** and **5** dispersed in dichloromethane (DCM) at the same concentration of 0.167 mg/ml, which were irradiated with a 365 nm ultraviolet (UV) lamp (note that polymer **4** and GNR **5** do not dissolve in DCM; they could be dispersed by sonication for the measurements but then quickly precipitate). While molecule **3** exhibits only a barely noticeable blue emission, polymer **4** shows a very bright cyan emission, and GNRs **5** exhibit no visible emission; photoluminescence spectra of all three products recorded with a 405 nm excitation light (Figure 2a) agree well with these observations. Thus, optical and photoluminescence data confirm a significant structural difference between products **3**, **4** and **5**.

Figure 2b illustrates structural transformations that occur by cyclodehydrogenation of polymer **4** to form GNRs **5**, as observed by ^{13}C NMR. In polymer **4** the solid state ^{13}C spectrum shows two resonances: one at 140 ppm and one at 130 ppm. All other resonances within the spectrum are spinning sidebands of these peaks at multiples of 8000 Hz (rotor spinning rate) from these two resonances. The peak at 140 ppm is the ipso carbon in aromatic ring- sp^2 hybridized carbons attached to other carbons. The peak at 130 ppm is from sp^2 hybridized carbons attached to protons. Polymer **4** loses these protons in the Scholl reaction to form **5**. Most carbons within **5** are bonded to other carbons, which broadens the signal to the average

resonance at 130 ppm. Again all the other peaks in the ^{13}C spectrum for **5** are spinning sidebands at the rotor resonance period (8000 Hz).

We also confirmed the successful transformation of the polymer **4** to GNR **5** by scanning tunneling microscopy (STM), see Figure 2c. Bottom left panel in Figure 2c shows an STM image of a polymer **4** deposited on a Au (111) single crystal. In accordance with the atomic structure of the polymer, it demonstrates regions of high electron density that correspond to molecular fragments shown by the red circle in Figure 2c. Furthermore, the polymer does not appear to be flat, which is in a good agreement with prior works: it was reported that phenyl groups of a polymer deposited on a gold substrate are tilted with respect to the surface and thus result in bright features in STM images.²⁶ In contrast to the polymer **4**, GNRs **5** appear to be perfectly flat on a Au (111) substrate, and the electron density is evenly distributed along the ribbon, which is expected for a fully aromatic system (see bottom right panel in Figure 2c and Figure 2d). The structure of the ribbons observed in these STM images is in a perfect agreement with the atomic structure of a GNR **5**.

Since these GNRs were deposited on a Au (111) single crystal in air from a toluene solution, it is inevitable that some solvent residues and other surface adsorbates will remain on the gold surface even in the high vacuum STM chamber. Thus, we attribute occasional white spots in STM images reported in this work to such adsorbates. Also, it should be noted that in order to prepare a sample for the STM analysis the GNRs should be heavily sonicated in an appropriate solvent, such as toluene, to be well dispersed; see SI for details. However, sonication is known to cut GNRs that are even 1-2 orders of magnitude wider than the ones reported in this work.¹⁴ Therefore, Figure 2d and similar STM images of heavily sonicated ribbons cannot be used to assess the lengths of these GNRs in a solution.

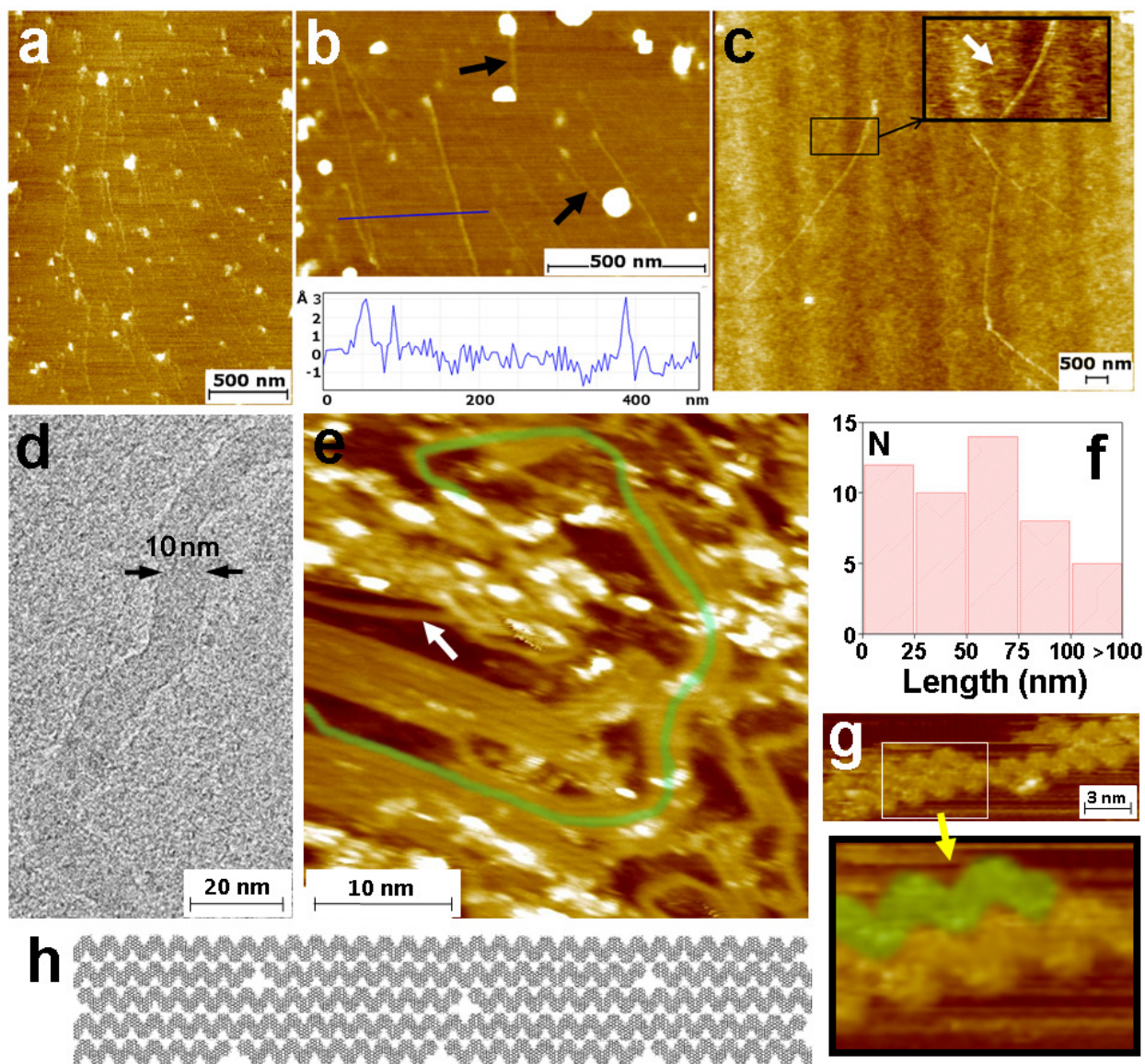


Figure 3. Microscopy characterization of GNRs. (a, b) AFM images of GNRs deposited on mica. Bottom panel in (b) shows the height profile along the blue line. (c) AFM image of GNRs deposited on a Si/SiO₂ substrate. (d) HRTEM image of a GNR nanobelt. (e) STM image of GNRs deposited on a Au(111) single crystal and annealed under vacuum at 40 °C for 20 min inside the STM chamber prior to imaging. The GNR highlighted in green is ~ 80 nm long. (f) Size distribution of the lengths of individual GNR observed in multiple STM images. (g) STM image showing arrangement of GNRs. In a magnified part one GNR is highlighted in green for

the sake of clarity. **(h)** A proposed structure of a GNR nanobelt. Note that this schematic does not represent the actual lengths of individual GNRs.

If the ribbons are not heavily sonicated but dispersed in toluene in milder conditions (see SI for details), deposited on a substrate and imaged by atomic force microscopy (AFM) upon drying, a very different morphology of GNRs is observed. Figure 3a-c show representative AFM images of GNRs deposited on a freshly cleaved surface of mica and on a Si/SiO₂ substrate, respectively; additional images are provided in SI. Observed in such images are elongated structures that are thin and remarkably long, many of them have lengths $> 1 \mu\text{m}$. Because of their large size, we could not determine the molecular mass of these structures by mass spectrometry. These structures could be mistaken for individual GNRs, but we demonstrate below that these structures are actually “nanobelts” of GNRs attached in a side-by-side fashion. The structure of these nanobelts was determined by a combination of microscopy techniques, such as AFM, high-resolution transmission electron microscopy (HRTEM) and STM.

Using AFM we can precisely determine the heights of such GNR nanobelts. The bottom panel in Figure 3b shows a representative height profile across two of these nanobelts, one of which is folded. Both nanobelts have a height of about 3 \AA , which is very close to the interlayer spacing in graphite (3.35 \AA).⁴⁷ We have measured height profiles in different AFM images for over 80 such nanobelts (several additional images are shown in SI), and in all cases we have observed heights $< 5 \text{ \AA}$. This means that these nanobelts are not stacks of GNRs, because their thickness corresponds to the thickness of a single graphene ribbon.

The inset in Figure 3c shows two GNR nanobelts that have a similar height of about $\sim 4 \text{ \AA}$ but visibly different widths (the narrower nanobelt is indicated by the white arrow). While

AFM cannot be used for a precise measurement of widths of these GNR nanobelts because of the tip curvature effect, such information could be obtained by HRTEM. Figure 3d shows a typical HRTEM image of a GNR nanobelt that has a width ~ 10 nm, which corresponds to 5-6 GNRs arranged side by side. Other GNR nanobelts observed in HRTEM images had widths from 7 to 14 nm.

To gain further insights into the structure of these GNR nanobelts, we used a toluene dispersion of GNRs that was only mildly agitated and refluxed to prepare a sample for the STM analysis. The sample was annealed at 40 °C for 20 min in vacuum inside the STM chamber prior to imaging to remove some of the residual solvent molecules and atmospheric adsorbates; a typical STM image is shown in Figure 3e. In this series of experiments we could not resolve fine structural features of GNRs like in Figure 2d, but numerous sub-2-nm strands that we attribute to individual ribbons are clearly visible; one of these ribbons is indicated by the white arrow. Such images confirm that GNRs indeed tend to form side-by-side assemblies that comprise 3-7 individual ribbons.

Using Figure 3e and a few similar STM images it was also possible to size individual GNRs that were not heavily sonicated in a solution. We found *ca.* 50 GNRs for which we could observe both ends and measured their lengths; the resulting size distribution is shown in Figure 3f. Some GNRs were > 50 nm long (for example, the GNR highlighted in green in Figure 3e is ~ 80 nm long), and several were > 100 nm long (see SI); such GNRs are long enough to bridge electrodes fabricated by standard electron beam lithography (EBL) technique⁴¹ (nanogaps as small as 10 nm with high aspect ratios could be fabricated by some modified EBL-based techniques⁴²).

Higher magnification STM images reveal the actual arrangement of individual GNRs in nanobelts. Figure 3g shows that when GNRs are arranged in a side-by-side fashion, the protrusions of one ribbon perfectly fit into the grooves of another one. Thus, based on the results of AFM, HRTEM and STM we conclude the observed GNR nanobelts consist of several ribbons attached side by side as shown in Figure 3h. At the moment it remains unclear if these structures exist in solution or form directly on a substrate by capillary forces during the solvent evaporation; it is also unclear if this side-by-side attachment is the only possible type of GNR assembly, or some of the ribbons in certain conditions also assemble via the π - π stacking or form “slanted” structures;⁴⁸ these questions will be answered in the future studies.

Figure 3a shows these GNR nanobelts span from the bottom part of the image to its top left corner; similarly aligned nanobelts are observed in panel (b). The GNR nanobelts were possibly straightened and partially aligned in the contact angle between a solution droplet and surface of a substrate during the solvent drying. Possible alignment of GNR nanobelts could streamline the device fabrication in future studies.⁴⁹ Furthermore, since GNR-based electronic devices are typically fabricated on Si/SiO₂ substrates,^{6-10, 14, 15, 18, 20, 21} it is important that these GNR nanobelts, although only a few angstroms thick, could be visualized by AFM not only on atomically flat mica, but also on substrates with a rougher surface, such as Si/SiO₂ (Figure 3c).

Because of their large size, some of these GNR nanobelts could aggregate or entangle. For example, the black arrows in Figure 3b shows two nanobelts with entangled ends; the entangled parts of the GNR nanobelts look like white spots in the AFM image. We have occasionally observed similar white spots at the ends and even in the middle of some nanobelts in other AFM images (see SI). Some of these nanobelts are fully entangled and appear as larger

white spots in AFM images (Figure 3a,b). However, the majority of nanobelts in these AFM images appear to be straightened and not entangled.

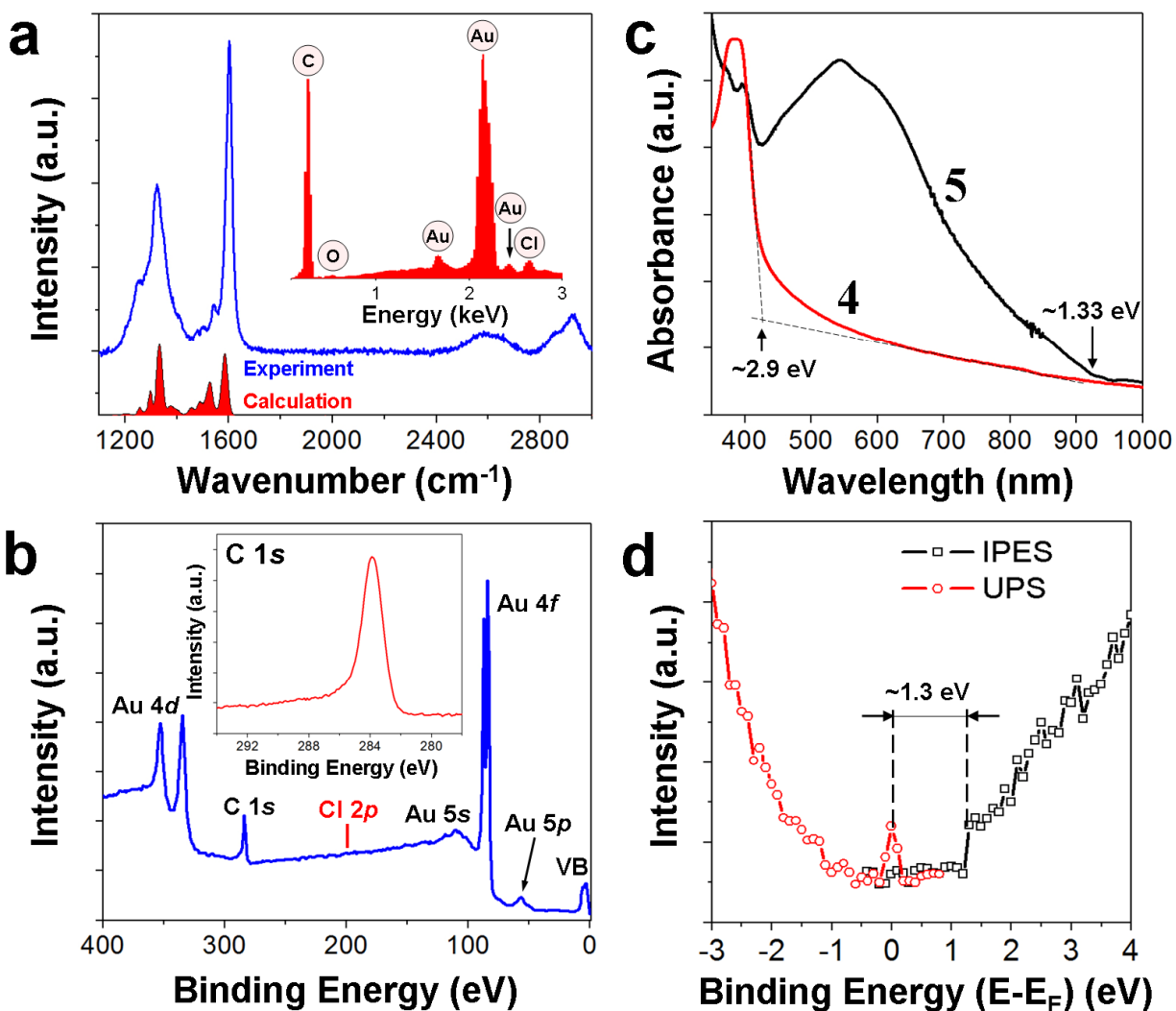


Figure 4. Spectroscopic characterization of GNRs. **(a)** Raman spectrum. The inset shows the EDX spectrum of GNRs deposited on a gold substrate. **(b)** XPS survey spectrum of GNRs deposited on a gold substrate. The inset shows the XPS C1s spectrum of the same sample. **(c)** UV-vis-NIR absorption spectra of polymer **4** (red) and GNRs **5** (black) suspended in DMF by sonication. **(d)** UPS/IPES spectrum of GNRs on a gold substrate.

We have further characterized GNRs by several spectroscopic techniques. Figure 4a demonstrates a Raman spectrum, where the most intense lines around 1300 cm^{-1} and 1600 cm^{-1} , typically referred to as D- and G-bands, respectively,⁵⁰ show an apparent fine structure. This pattern is characteristic for all-benzene polycyclic aromatic hydrocarbons (PAHs); the relative intensities and positions of the lines depend on the molecular structure of a PAH.^{51, 52} We performed a simulation of the GNR **5** Raman spectrum and found a good agreement between the calculated and experimentally observed peak positions. In accordance with the experiment, the calculated spectrum predicts the fine structure of three separate peaks at the left shoulder of the G band but no additional peaks at the right shoulder. Similarly, the calculated spectrum predicts a small peak at the right shoulder of the D band and larger peaks at the left shoulder; these features are also observed experimentally. Due to the high sensitivity of the Raman spectroscopy to the disorder in carbon materials, the experimental observation of the fine structure in the Raman spectrum of GNRs could be considered as another evidence to the high structural quality of the synthesized material.

The inset in Figure 4a shows an EDX spectrum of GNRs deposited on a gold foil. Except for the strong Au peaks that are originated from the substrate, the only foreign peak observed is the low intensity Cl line (atomic ratio C:Cl \sim 300:1), which could be caused by either Cl^- ions adsorbed on ribbons after the HCl washing in the last reaction step or dichloromethane that was used for the sample preparation (see SI). We also mark the position of the O peak, demonstrating that only a negligible amount of oxygen, that is probably caused by atmospheric adsorbates, could be detected. No other impurity elements from different reagents and catalysts used in the GNR synthesis were detected.

Interestingly, that chlorine impurities, which were observed by EDX, were not detected by the X-ray photoelectron spectroscopy (XPS) analysis of the same sample (Figure 4b), possibly because the XPS analysis was performed in higher vacuum compared to the EDX, which facilitated the desorption of dichloromethane residues. The XPS survey scan shown in Figure 4b demonstrates only the peaks associated with the GNRs and the gold substrate. The inset in Figure 4b shows the XPS C1s spectrum where only a single sharp component at 284.5 eV corresponding to the sp^2 carbons is observed. No other peaks corresponding to the carbon in different oxygen-containing functionalities⁵³ are observed, further confirming that these GNRs are chemically pure and do not oxidize in air.

Since we have fabricated bulk quantities of GNRs, we could measure their bandgap spectroscopically. Figure 4c shows a UV-vis-NIR spectrum of the dispersion of ribbons sonicated in N,N-dimethylformamide (DMF) (along with N-methyl-2-pyrrolidone (NMP), DMF was found to be one of the most effective dispersion medium for GNRs, see SI for details); a spectrum of polymer **4** is shown for comparison. The GNR spectrum exhibits a strong absorption in the UV and visible region, and an absorption edge in NIR. The absorption onset at ~ 930 nm corresponds to the optically measured bandgap in GNRs of ~ 1.33 eV.^{40, 54} This value is significantly higher than other experimental bandgap values reported for GNRs fabricated by top-down approaches;^{6-9, 18} it is close to the calculated value of 1.6 eV (Figure 1b), and higher than that in silicon (1.1 eV).

To better assess the bandgap in these GNRs, we have performed ultraviolet photoemission spectroscopy (UPS) and inverse photoemission spectroscopy (IPES). The measurements were performed on a pressed pellet of GNRs that was 0.75 cm in diameter and ~ 0.5 mm thick; the pellet was placed on a Au(111) surface that was also used for the

spectrometer calibration (see SI for details.) The combined UPS/IPES measurements were undertaken to study the molecular orbital placement of both occupied and unoccupied orbitals in GNRs. In both UPS and IPES measurements, the binding energies were referenced with respect to the Fermi edge of gold in intimate contact with the samples studied, so as to correctly establish the chemical potential free of all instrumental errors. The data are shown in terms of $E-E_F$, thus making occupied state energies negative. The UPS/IPES data are shown in Figure 4d; qualitatively similar energy spectra were previously measured by the scanning tunneling spectroscopy (STS) for other GNRs synthesized by a surface-assisted approach.^{27, 30} We have observed a bandgap of ~ 1.3 eV, which is in a good agreement with the results of optical spectroscopy. The observed peak in the UPES spectrum (occupied density of states) that appears at the Fermi level could be a result of the fact that these GNRs have large effective mass (as expected) leading to a large density of states at the top of the valence band maximum. Narrow occupied states of heavy effective mass could also emerge from edge states that are a direct result of the restricted dimensionality of the GNR; similar peaks in STS spectra of other GNRs, were also interpreted as the edge states.^{55, 56} This occupied state observed in the UPES spectrum at the Fermi level may in fact be more narrow than plotted in Figure 4d, as there is finite instrumental resolution of more than 70 meV and the measurements done at the elevated temperature of 300 K, adding a thermal broadening widths to the GNR states observed; in addition to any lifetime broadening and band dispersion broadening effects. In spite of an extremely low density of occupied states in the vicinity of the chemical potential, this material is p-type, *i.e.* the LUMO is well above the chemical potential (E_F).

The 1.3 eV bandgap of GNRs **5** is close to the optical bandgap of 1.12 eV reported for other solution-synthesized GNRs;⁴⁰ as expected, the value found in the present work is slightly

larger because the GNRs **5** are narrower than the ribbons synthesized in Ref. 40. However, the 1.3 eV bandgap is substantially lower than the values reported in the studies of individual GNRs synthesized by the surface-assisted approach on gold substrates.^{27, 28, 33, 34} For example, a significantly larger band a bandgap of 3.1 ± 0.4 eV was recently reported for the same GNRs **5** synthesized on Au(788) by the surface-assisted approach;³⁴ this value is much higher than the value of ~ 1.3 eV found in this work for GNRs **5**, and even larger or comparable to the bandgap of the precursor polymer **4** (~ 2.9 eV) determined from the optical measurements (Figure 4c). A possible explanation for these differences is the fact that the characterization of solution-synthesized GNRs (or polymer precursors), such as absorption spectroscopy and UPS/IPES, is performed on bulk samples where GNRs (or precursor polymers) are heavily aggregated, whereas prior measurements were performed on isolated GNRs on a gold substrate.³⁴ Aggregation effects were previously shown to affect the absorption spectra of polycyclic aromatic hydrocarbon (PAH) molecules visibly reducing their apparent bandgaps.⁵⁷ Similarly, it is possible that the value of ~ 1.3 eV represents not an intrinsic bandgap of an individual GNR **5**, but a bandgap of a bulk GNR material. On the other hand, the results of the band structure measurements of GNRs on metallic substrates could be affected by the GNR-substrate interactions (for example, gold was shown theoretically⁵⁸ and experimentally⁵⁹ to cause the hole doping of graphene), which should also be taken into account when interpreting the data or comparing the results of different experiments. Even if the value of 1.3 eV represents the bandgap of a bulk GNR material, knowing this bandgap is very important, because of many potential bulk applications of synthetic GNRs, such as photovoltaics, printed electronics and composite materials. Additional studies of the band structures of different synthetic GNRs in general and GNR aggregation effects in particular are definitely in order.

In summary, we have demonstrated a novel bottom-up approach that yields gram quantities of high-aspect-ratio GNRs, which are only ~ 1 nm wide and have atomically smooth armchair edges. The important characteristics of these GNRs are their large bandgap of about 1.3 eV, their large lengths, the ease with which they can be deposited on any substrate, and their ability to be visualized by conventional microscopy techniques. Although we have demonstrated the synthesis of only one type of GNRs, we believe that GNRs with other structures could also be synthesized by a similar bottom-up approach. Further device studies will reveal if these GNRs with large electronic bandgaps could be an alternative to silicon in high on-off ratios FETs, logic gates, and photovoltaic devices.

Methods

Complete synthetic details are given in SI. Briefly, the synthesis of monomer precursor **3** involved brominating 2,7-dibromophenanthrene-9,10-dione using N-bromosuccinimide (NBS) to achieve **1** in a quantitative yield. Reacting **1** and 1,3-diphenylacetone using potassium hydroxide as a base resulted in **2**. We found that the yield of **2** depends on the amount of solvent used. To synthesize **3** we followed the procedure by Saleh *et al.*⁶⁰ with some modifications; the compound was synthesized by [2+4] Diels-Alder cycloaddition of **2** and diphenylacetylene. The crude material **3** was slowly re-crystallized in a minimal amount of tetrahydrofuran at -20 °C. The yield was higher when the crude material was purified by column chromatography using silica as a stationary phase and hexane/ethyl acetate as a mobile phase. Column chromatography was not a preferable purification method when the process was scaled up to a gram scale. Yamamoto coupling using Ni⁰ was employed to make triphenylene-based polymer **4**. We found that it was necessary to use a large excess of Ni catalyst: 1.5 to 3 molar equivalences of excess Ni⁰ were

used to obtain **4**. GNRs were synthesized by a Scholl reaction that involves cyclodehydrogenation of the polymer **4** using iron (III) chloride to achieve a black material **5**.

The DFT calculations of the GNR band structure were performed by using a CASTEP package; we used PBE functional with ultrasoft pseudopotentials. The Raman spectrum was simulated using the Quantum Espresso package.⁶¹ ¹H and ¹³C NMR was performed on Bruker 300 MHz, 400 MHz and 600 MHz NMR instruments. Magic angle spinning was performed at 600 MHz with the spinning speed of 8 kHz. AFM analysis was performed on a Digital Instruments Nanoscope IIIa Dimension 3100 system. AFM imaging was performed using Bruker RTESPA AFM probes (part # MPP-11120-10). Raman spectrum of GNRs was recorded on a Thermo Scientific DXR Raman Microscope with a 532 nm laser. UV-vis-NIR spectroscopy of performed on a Shimadzu UV-2401PC instrument. Photoluminescence spectra were obtained using a Shimadzu RF-5301PC instrument. Molecule **3** was characterized by MS using a Micromass GCT mass spectrometer with an electron impact (EI) direct probe that was heated up to 200 °C. Polymer **4** and GNRs **5** were analyzed by matrix-assisted laser desorption/ionization (MALDI) MS on an Applied Biosystems Voyager DE-Pro instrument using a tetracyanoquinodimethane (TCNQ) matrix. EDX analysis was performed on a FEI Nova NanoSEM 450 scanning electron microscope equipped with an Oxford Instruments EDX system. HRTEM images of GNRs were obtained using an FEI Tecnai Osiris transmission electron microscope. XPS was performed on a PHI Quantera SXM scanning X-ray microprobe. UPS/IPES measurements were performed using the home-build setup described elsewhere.⁶² An Omicron low-temperature scanning tunneling microscope (LT-STM) with an electrochemically etched W tip, kept at a base pressure of 10^{-10} Torr, was used for the STM imaging. Details on

sample preparation and data acquisition parameters for different characterization techniques are given in SI.

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Author contributions

T.H.V. and A.S. conceived the experiments. T.H.V. developed the synthetic route to GNRs, performed all reactions, and most of characterization of GNRs, including NMR, UV-vis-IR, photoluminescence and Raman spectroscopy, and AFM. M.D.M. assisted with NMR and interpreted the NMR data. E.B. and M.S. performed AFM and processed the images. M.S. performed EDX analysis and some of the UV-vis-IR measurements. D.K. and A.E. performed STM and analyzed the data. L.K. and P.A.D. performed PES/IPES and interpreted the data. P.W. assisted with XPS and Raman spectroscopy. T.H.V. and A.S. co-wrote the paper. A.S. supervised the project.

Additional information

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