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Covalent Functionalization of Surfactant-Wrapped Graphene Nanoribbons

Yu Zhu, Amanda L. Higginbotham, and James M. Tour*

Departments of Chemistry and Mechanical Engineering and Materials Science and the Smalley Institute for Nanoscale Science and Technology, Rice University, MS 222, 6100 Main Street, Houston, Texas 77005

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Using diazonium chemistry, two different covalent functionalization methods for graphene nanoribbons (GNRs) were developed. In addition to direct diazonium salt addition, which has been reported previously for functionalization of graphene sheets and single-walled carbon nanotubes, an in situ route using an organic nitrite was successfully applied. This new method broadens the possibilities of functionality type since anilines can be used instead of preprepared diazonium salts. The resulting functionalized GNRs (f-GNRs) are readily soluble in organic solvents such as *N,N*-dimethylformamide and *N*-methyl-2-pyrrolidinone, which increases their solution processability. The f-GNRs were also found to be in a reduced state, with minimal sp^2 carbon disruption, while keeping the ribbon shape. These organic-soluble ribbons might find applications in composites and thin film materials.

Introduction

Graphene, a 2D atomic layer of sp^2 hybridized carbon arranged in a hexagonal network, has been regarded as a promising material for nanoelectronics owing to its high crystallinity and interesting semimetal electronic properties.[1−3] Graphene nanoribbons (GNRs), which gradually transform from semiconducting to semimetals as their width increases,[4−7] represent a particularly versatile variety of graphene. Methods for producing microscopic quantities of few-layer graphene nanoribbons include microfabrication on graphite surfaces,[7] exfoliation of bulk graphite in the presence of surfactants,[8] or plasma etching of multiwalled carbon nanotubes (MWCNTs) partially imbedded in a layer of protective polymer.[9] Chemical syntheses routes have also been developed which produce short ribbons up to 12 nm in length.[10] The first reported method for producing bulk quantities of GNRs was through a chemical vapor deposition (CVD) growth process that resulted in ribbons containing multiple layers of graphene with a kinked morphology.[11] Our group developed a high-yielding solution-based bulk method that produces single- and few-layer GNRs from MWCNTs via oxidative longitudinal unzipping.[12] The high surface area, high aspect ratio, and interesting electronic properties of GNRs render them promising candidates for applications in composite materials,[2,13,14] field-effect transistors,[15,16] solid state gas-sensors,[17] spin-valve and hydrogen storage materials,[18] energy-storage materials,[19] and liquid crystal devices.[20]

The GNRs produced from the solution-based oxidative unzipping process,[12] although with quantitative yield, have highly oxidized planes. In order to restore the ribbons to a more graphene-like structure, subsequent chemical reduction with hydrazine must be carried out. Though some of the electrical conductivity is restored

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*E-mail: tour@rice.edu.

(1) Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Katsnelson, M. I.; Grigorieva, I. V.; Dubonos, S. V.; Firsov, A. A. *Nature* **2005**, *438*, 197–200.
(2) Geim, A. K.; Novoselov, K. S. *Nat. Mater.* **2007**, *6*, 183–191.
(3) Zhang, Y. B.; Tan, Y. W.; Stormer, H. L.; Kim, P. *Nature* **2005**, *438*, 201–204.
(4) Areshkin, D. A.; Gunlycke, D.; White, C. T. *Nano Lett.* **2007**, *7*, 204–210.
(5) Son, Y. W.; Cohen, M. L.; Louie, S. G. *Phys. Rev. Lett.* **2006**, *97*, 216803.
(6) Nakada, K.; Fujita, M.; Dresselhaus, G.; Dresselhaus, M. S. *Phys. Rev. B* **1996**, *54*, 17954–17961.
(7) Han, M. Y.; Oezyilmaz, B.; Zhang, Y.; Kim, P. *Phys. Rev. Lett.* **2007**, *98*, 206805.
(8) Li, X.; Wang, X.; Zhang, L.; Lee, S.; Dai, H. *Science* **2008**, *319*, 1229–1232.
(9) Jiao, L.; Zhang, L.; Wang, X.; Diankov, G.; Dai, H. *Nature* **2009**, *458*, 877–880.
(10) Yang, X. Y.; Dou, X.; Rouhanipour, A.; Zhi, L. J.; Rader, H. J.; Mullen, K. *J. Am. Chem. Soc.* **2008**, *130*, 4216–4217.
(11) Campos-Delgado, J.; et al. *Nano Lett.* **2008**, *8*, 2773–2778.
(12) Kosynkin, D. V.; Higginbotham, A. L.; Sinitskii, A.; Lomeda, J. R.; Dimiev, A.; Price, B. K.; Tour, J. M. *Nature* **2009**, *458*, 872–876.
(13) Stankovich, S.; Piner, R. D.; Chen, X.; Wu, N.; Nguyen, S. T.; Ruoff, R. S. *J. Mater. Chem.* **2006**, *16*, 155–158.
(14) Stankovich, S.; Dikin, D. A.; Dommett, G. H. B.; Kohlhaas, K. M.; Zimney, E. J.; Stach, E. A.; Piner, R. D.; Nguyen, S. T.; Ruoff, R. S. *Nature* **2006**, *442*, 282–286.
(15) Hill, E. W.; Geim, A. K.; Novoselov, K.; Schedin, F.; Blake, P. *IEEE Trans. Magn.* **2006**, *42*, 2694–2696.
(16) Heersche, H. B.; Jarillo-Herrero, P.; Oostinga, J. B.; Vandersypen, L. M. K.; Morpurgo, A. F. *Nature* **2007**, *446*, 56–59.
(17) Schedin, F.; Geim, A. K.; Morozov, S. V.; Hill, E. W.; Blake, P.; Katsnelson, M. I.; Novoselov, K. S. *Nat. Mater.* **2007**, *6*, 652–655.
(18) Sofo, J. O.; Chaudhari, A. S.; Barber, G. D. *Phys. Rev. B* **2007**, *75*, 153401.
(19) Stoller, M. D.; Park, S. J.; Zhu, Y. W.; An, J. H.; Ruoff, R. S. *Nano Lett.* **2008**, *8*, 3498–3502.
(20) Blake, P.; Brimicombe, P. D.; Nair, R. R.; Booth, T. J.; Jiang, D.; Schedin, F.; Ponomarenko, L. A.; Morozov, S. V.; Gleeson, H. F.; Hill, E. W.; Geim, A. K.; Novoselov, K. S. *Nano Lett.* **2008**, *8*, 1704–1708.

after reduction, the GNRs were found to aggregate and precipitate from solution very quickly if surfactant is not used. This hinders the processability of GNRs in reduced form. Previous work in our group has shown that covalent functionalization can be successfully carried out on chemically converted graphene sheets[21] and carbon nanotubes[22−25] in order to increase the processability of those materials. In this work, two different covalent functionalization methods were developed for GNRs. In addition to direct diazonium salt addtion, an in situ route using an aniline and organic nitrite was successfully applied. The resulting functionalized graphene nanoribbons (f-GNRs) are readily soluble in organic solvents such as *N,N*-dimethylformamide (DMF) and *N*-methyl-2-pyrrolidinone (NMP). The f-GNRs were also found to be in the reduced state, with minimal sp^2 carbon disruption, while also keeping the ribbon shape.

Experimental Procedures

Materials. 4-Nitroaniline, 4-chloroaniline, 4-bromoaniline, and 2,4-dimethoxyaniline were obtained from Sigma-Aldrich or Acros Organics and used without further purification. Anlines were converted into the corresponding diazonium tetrafluoroborate via diazotization in aqueous hydrochloric acid followed by addition of fluoroboric acid to precipitate the arenediazonium tetrafluoroborate salt, following the procedure described in the literature.[26] Fluoroboric acid, sodium nitrite, isoamyl nitrite, hydrazine hydrate, and acetonitrile were purchased from Fisher or Acros Organics and were used as received. Graphene nanoribbons were prepared from Mitsui MWCNTs using the procedure recently reported by our group.[12]

General Procedure for the Synthesis of Functionalized GNRs (Route I). The as-prepared oxidized graphene nanoribbons[12] were wrapped in sodium dodecylsulfate (SDS) surfactant by gently stirring 30 mg of GNRs in 30 mL 1 wt % aqueous SDS for 1 h, followed by bath sonication of the solution for 10 min (Cole Parmer ultrasonic cleaner, model 08849-00). The suspension was then filtered through a 5-cm plug of glass wood and transferred to an Erylenmeyer flask. We have found that gentle stirring or short bath sonication of the nanoribbons is fine; however, use of high shear homogenization, probe sonication, or cup-horn sonication will result in shortened GNRs. Chemical reduction was carried out by adding 30 μL of concentrated NH_4OH (0.444 mmol) followed by 30 μL of $N_2H_4 \cdot H_2O$ (98%, 0.606 mmol). The reaction mixture was heated at 95 °C for 1 h (no stirring). The heating bath was then removed, and the reaction mixture was allowed to cool to room temperature. Functionalization was carried out by predissolving the solid diazonium salt (10 mmol, 4 equiv per nanoribbon carbon) into a minimum amount of water. This solution was then added dropwise with stirring to the reduced nanoribbon solution. The reaction contents were allowed to stir for 1 h at room temperature. The mixture was then poured into 100 mL acetone to coagulate the f-GNRs. This mixture was filtered through a 0.45 μm PTFE (Teflon) membrane, washed with water and acetone (3×), and resuspended in DMF to remove SDS and excess diazonium salt. This was followed by filtration (0.45 μm PTFE) and copious washing of the filter cake with acetone. The resulting solid was dried at 70 °C in a vacuum oven overnight typically yielding 36−38 mg of f-GNRs.

General Procedure for the Synthesis of Functionalized GNRs (Route II). The surfactant wrapping and hydrazine reduction of the ribbons (starting from 30 mg oxidized graphene nanoribbons) were performed as described above. Functionalization was carried out in a 250 mL three-neck flask to which the aniline (10 mmol, 4 equiv per nanoribbon carbon, predissolved in 30 mL acetonitrile) and 30-mL reduced graphene ribbon solution (1 mg/mL GNRs) were added. To this mixture, isoamyl nitrite (10 mmol) was slowly added dropwise under nitrogen atmosphere. The reaction mixture was heated with stirring to 70 °C for 12 h. The reaction was then cooled, and the suspension filtered through a 5 cm plug of glass wool. The filtrate was then filtered through a 0.45 μm PTFE membrane. The filter cake was washed with acetone and resuspended in DMF and filtered again, and the resulting filter cake was washed with copious amounts of DMF, water, and acetone. Though soluble in DMF, the GNRs do not penetrate the filter membrane. The product was collected and dried in vacuo at 70 °C for 24 h before it was used for any characterization typically yielding 25−35 mg of f-GNRs.

Characterization. Products were characterized by ultraviolet-visible spectroscopy (UV-vis), thermogravimetric analysis (TGA), Raman spectroscopy, FTIR spectroscopy, X-ray photoelectron spectroscopy (XPS), cyclic voltammetry (CV), and atomic force microscopy (AFM).

TGA was performed, after drying the sample at 110 °C for 20 min, from room temperature to 900 at 10 °C/min under argon. Raman spectra of powder samples were recorded with a Renishaw Raman scope using a 633 nm argon laser. In order to verify functionalization of the GNRs, the ratio of the diamondoid (D) to the graphitic (G) band (D:G ratio) was calculated by applying a Lorentz fit to the spectrum after baseline correction and integrating the areas of the D and G bands. XPS was carried out on a PHI Quantera SXM scanning X-ray microprobe with a base pressure of 5×10^{-9} Torr. As an X-ray source, an Al cathode at 100 W was used with a pass energy of 26.00 eV, 45° takeoff angle, and a 100 μm beam size. Low resolution survey scans as well as high resolution scans of C, O, N, Cl (for **2a** and **3a**), and Br (for **2b** and **3b**) were taken. C1s spectra were normalized and shifted to standard positions. FTIR spectra were obtained either with an attenuated total reflectance accessory (ATR-IR) or with a prepared KBr/GNR pellet. AFM samples were prepared by spin coating the sample from DMF onto a freshly cleaved mica surface. AFM images were obtained using tapping mode with a tapping frequency of 1.5 Hz. For CV, a thin film of the functionalized GNRs was cast from a DMF solution on a glass carbon electrode and cycled in degassed, anhydrous acetonitrile containing 0.1 M tetrabutylammonium hexafluorophosphate as the electrolyte. Counter and reference electrodes were platinum and silver, respectively. The voltage data was corrected using ferrocene, the scan rate was 25 mV s^{-1}, and the temperature was 20 °C.

Results and Discussion

Owing to the high yield of individual nanoribbons, chemical unzipping of carbon nanotubes to

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(21) Lomeda, J. R.; Doyle, C. D.; Kosynkin, D. V.; Hwang, W. F.; Tour, J. M. *J. Am. Chem. Soc.* **2008**, *130*, 16201–16206.

(22) Bahr, J. L.; Yang, J.; Kosynkin, D. V.; Bronikowski, M. J.; Smalley, R. E.; Tour, J. M. *J. Am. Chem. Soc.* **2001**, *123*, 6536–6542.

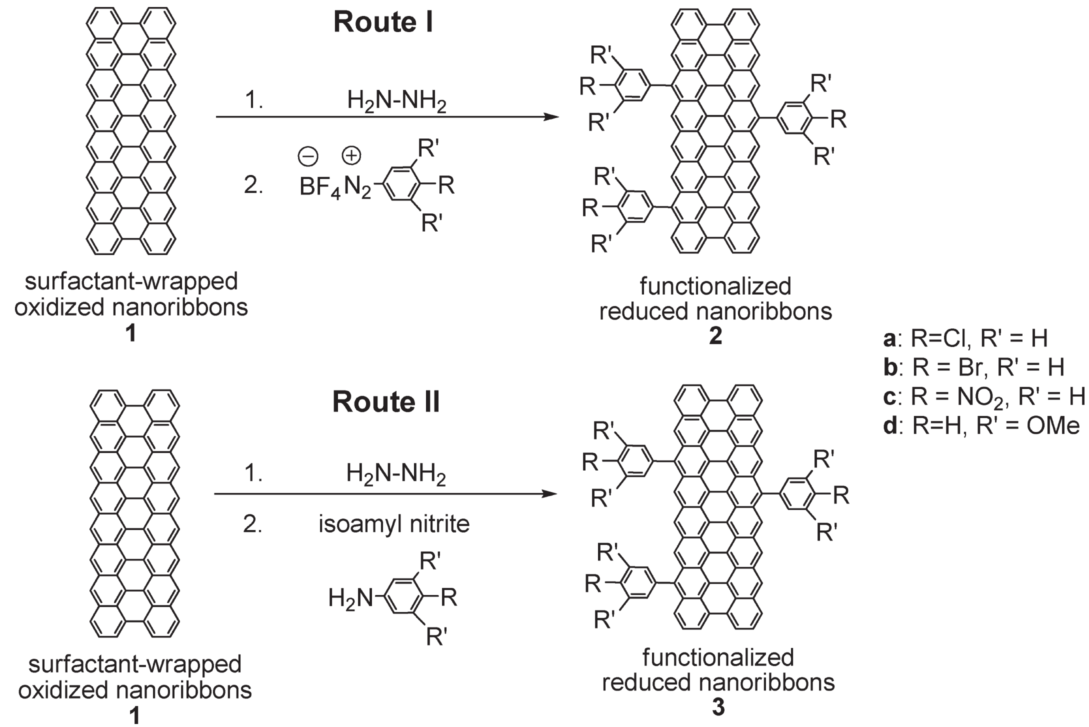
(23) Bahr, J. L.; Tour, J. M. *Chem. Mater.* **2001**, *13*, 3823–3824.

(24) Dyke, C. A.; Tour, J. M. *Nano Lett.* **2003**, *3*, 1215–1218.

(25) Price, B. K.; Tour, J. M. *J. Am. Chem. Soc.* **2006**, *128*, 12899–12904.

(26) Curtin, D. Y.; Ursprung, J. A. *J. Org. Chem.* **1956**, *21*, 1221–1225.

Scheme 1. Syntheses Routes I and II for the Production of f-GNRs[a]



[a] The oxidized starting material nanoribbons (**1**) bear oxygen-containing functionalities such as carbonyls, carboxyls, epoxides, and hydroxyls (not shown). Covalent attachment of the aryl moieties is not limited to the edges of the nanoribbons as depicted for functionalized products **2** and **3**; attachment at the basal plane is also expected.

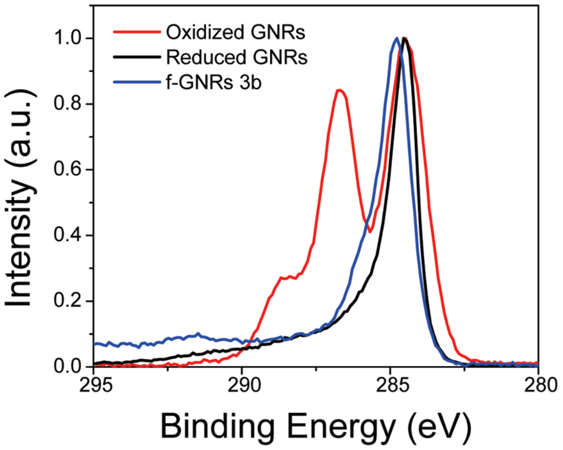


Figure 1. High-resolution XPS C1s spectra of oxidized GNRs (red), reduced GNRs (black), and f-GNRs **3b** (blue) showing significant loss of C—O and C═O groups after reduction.

graphene nanoribbons exhibits advantages over other methods.[9−11,27] The restoration of the ribbons to a graphene-like structure has been confirmed.[12] This procedure, as a high-throughput method, would likely be preferred for preparation of composites or transparent electrode materials where large quantities are required.

The two routes for functionalization are shown in Scheme 1. The reaction of GNRs with aryl diazonium salts (route I) was found to proceed similarly to the reaction of surfactant-wrapped, chemically converted graphene sheets with aryl diazonium salts.[21,28] While the in situ functionalization of GNRs using organic nitrite and aromatic amine (route II) has not yet been reported for graphene materials, it has been successfully applied to the functionalization of carbon nanotubes.[23,29]

Table 1. High-Resolution XPS Results of 2 and 3[a]

sample	atomic concentration (%) C	N	O	Cl	Br
2a	80.2	2.8	10.9	5.0	–
2b	77.5	5.5	11.4	–	5.6
2c	70.8	9.5	19.5	–	–
2d	73.6	3.9	22.5	–	–
3a	74.1	3.1	16.4	6.4	–
3b	79.6	3.5	14.3	–	2.6
3c	66.9	5.6	27.5	–	–
3d	65.4	3.0	31.6	–	–
Oxidized GNRs	52.0	1.3	35.8	–	–
Reduced GNRs	79.1	3.5	17.3	–	–

[a] A dash indicates an atomic concentration of $<0.5\%$ was detected by XPS.

X-ray photoelectron spectroscopy (XPS) was used to verify the success of functionalization reactions. Previous results for the chemical reduction of graphene nanoribbons indicated there was significant removal of oxygen groups by hydrazine treatment.[12] Similar results were observed by high resolution XPS C1s spectra of the f-GNRs, which show a significant decrease of signals at 286−288 eV, indicating the loss of C—O and C═O functionalities (Figure 1). The surface oxygen groups in GNRs were estimated to be 42%, while after treatment

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(27) Li, X.; Wang, X.; Zhang, L.; Lee, S.; Dai, H. *Science* **2008**, *319*, 1229–1232.

(28) Si, Y.; Samulski, E. T. *Nano Lett.* **2008**, *8*, 1679–1682.

(29) Dyke, C. A.; Tour, J. M. *J. Am. Chem. Soc.* **2003**, *125*, 1156–1157.

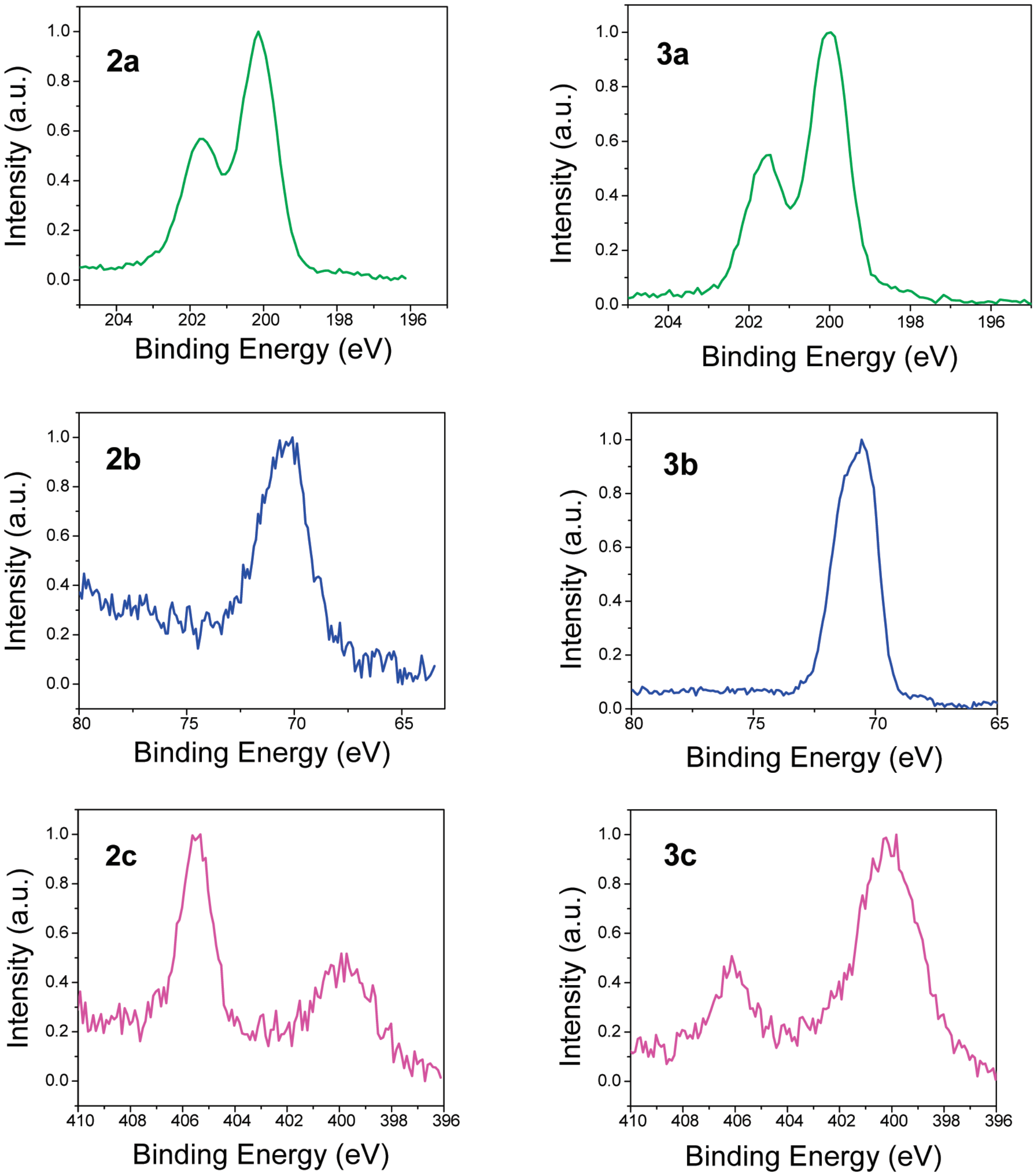

Figure 2. High-resolution XPS Cl2p spectra of **2a** and **3a** (top row), Br3d spectra of **2b** and **3b** (middle row), and N1s spectra of **2c** and **3c** (bottom row).

with hydrazine, the percentage of oxygen decreased to 16%.[12] Since these are ribbon structures, the high remaining edge carboxyl units will undergo little reductive loss. Depending on the functional groups, the surface oxygen in f-GNRs ranges from 11% to 32% (Table 1). A small portion of nitrogen content exists in all products, which can be attributed to hydrazones (except the N1s XPS spectra of **2c** and **3c**, which exhibit a significant contribution from the nitro group as well).[13,30] Upon treatment with the diazonium salts (route I) or with the in situ functionalization procedure (route II), a significant percentage of halogen markers (Cl or Br) were detected with very little accompanying nitrogen, implying that the surface has been successfully functionalized (Figure 2). Therefore, the data supports the conclusion that both routes resulted in successful functionalization. Similar to the previous report of functionalization of graphene sheets, the functionalized graphene nanoribbons were formed by covalent grafting of diazonium species.[21,31] High-resolution XPS of **2c** and **3c** show two signals for the N1s peak. The signal at 405 eV can be attributed to the nitro group (Figure 2). High resolution XPS of **2d** and **3d** show a broad C1s signal, which is partially due to the presence of the C—O bond, such as that found in a methoxy group on a substituted phenyl

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(30) Becerril, H. A.; Mao, J.; Liu, Z.; Stoltenberg, R. M.; Bao, Z.; Chen, Y. *ACS Nano* **2008**, *2*, 463–470.

(31) Bekyarova, E.; Itkis, M. E.; Ramesh, P.; Berger, C.; Sprinkle, M.; de Heer, W. A.; Haddon, R. C. *J. Am. Chem. Soc.* **2009**, *131*, 1336–1337.

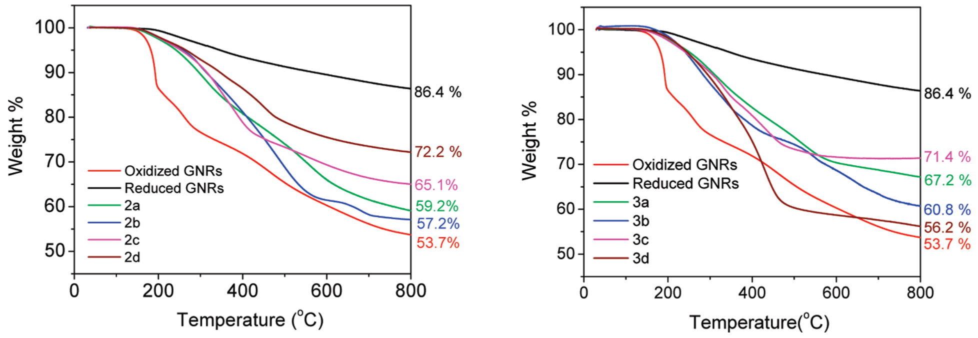

Figure 3. TGA thermograms of f-GNRs **2** (left) and **3** (right) compared to oxidized GNR starting material and reduced GNR with no functional group attached.

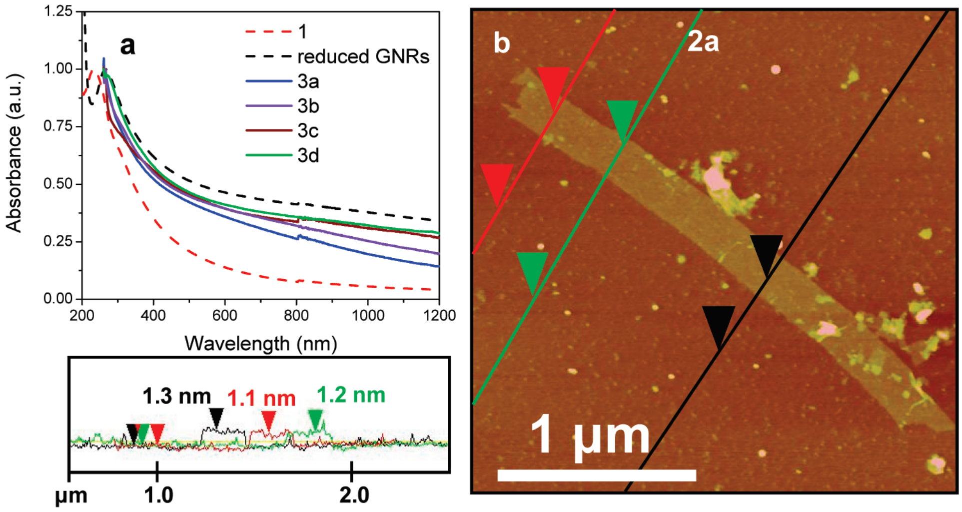

Figure 4. (a) UV-vis spectra of GNRs and f-GNRs. Spectra of **1** and reduced GNRs were measured in 1% SDS water solution. Spectra of **3a**−**3d** were measured in DMF. (b) AFM image of a single, > 3 μm long f-GNR from sample **2a**. The height data is given in the bottom left panel.

ring. The fitting of C1s (Supporting Information Figure S1) exhibits a peak from C—O (286.2 eV) as well as a residual signal from carboxylic acids C=O (287.7 eV).

Control experiments for both routes were conducted by adding chlorobenzene, instead of the analogous diazonium salt or aniline derivative, to the reduced GNR surfactant suspension. The typical workup procedure was then followed, and XPS analysis was done to ensure that the Cl detected in the functionalization reactions was present due to covalent attachment as opposed to physisorption and intercalation of chlorinated material between the ribbons. XPS analysis of the control sample detected < 0.1% atomic concentration of Cl at 200 eV. Hence, this confirms that functionalization was successful and that partial rearomatization of the nanoribbons occurred after hydrazine reduction, thus providing a suitable surface for aryl grafting of the diazonium species.[21,28]

TGA was used to determine the degree of functionalization of the f-GNRs, by comparing the weight loss of the functionalized samples to the weight loss of the oxidized GNR starting material and reduced-only GNRs. The TGA weight loss of the f-GNRs is presented in Figure 3; the mass loss of the f-GNRs is between 28 and 44%, which falls in the middle of the mass loss recorded for oxidized GNRs (46%)[12] and reduced GNRs with no attached functional groups (15%). This indicates that fewer volatile sidewall functionalities are present on the f-GNR surface compared with the oxidized starting materials. The reduced GNRs and the product of the control reaction were found to undergo less weight loss, which is due to the absence of functional groups. The defunctionalization of the f-GNRs is estimated to occur between 200 and 700 °C; from this data, it is estimated that there is approximately 1 functional group for every 20−50 nanoribbon carbons. This underscores the efficacy of the two functionalization methods described here and demonstrates that the two processes give equivalent degrees of functionalization.

The λ_{max} and relative intensities of the UV−vis absorption of the different GNR samples indicate the degree of π-conjugation present in the system; a highly conjugated system will have λ_{max} at higher wavelengths and an increased intensity of absorption over the entire spectrum (> 230 nm). The UV−vis spectra of the oxidized GNR starting material, reduced GNRs, and f-GNRs (**3**) are shown in Figure 4a. As expected, a bathochromic shift of λ_{max} and hyperchromicity over the entire range was observed after hydrazine reduction, indicating that electronic conjugation of the oxidized starting ribbons was restored.[32]

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(32) Li, D.; Mueller, M. B.; Gilje, S.; Kaner, R. B.; Wallace, G. G. *Nat. Nanotechnol.* **2008**, *3*, 101–105.

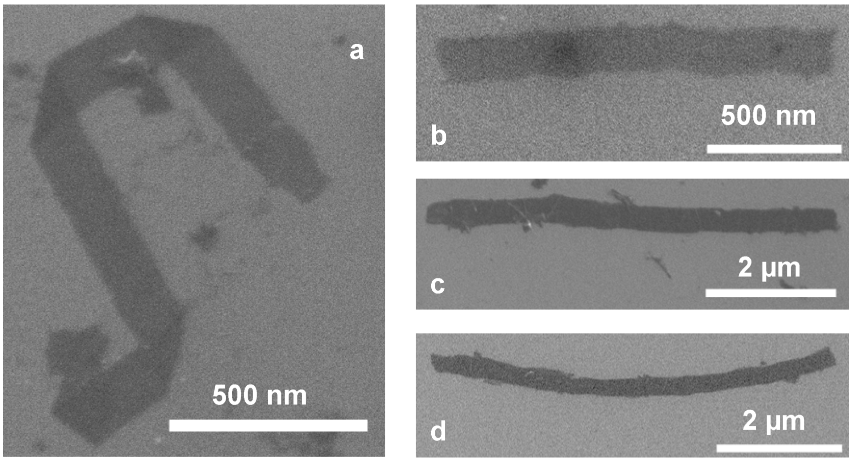

Figure 5. SEM images of f-GNRs from sample **2a**. A fresh DMF solution of f-GNRs was prepared and spin-coated onto a silicon surface, containing a 500 nm layer of SiO_2, prior to imaging. The f-GNRs shown in images a and b are single layers while those in c and d are few-layered stacks.

After functionalization, λ_{max} was hypsochromically shifted while the hypochromicity was maintained over the entire range (>230 nm); this indicates that the conjugated system was interrupted slightly by covalent aryl grafting. Although the functionalization decreased the aromaticity of the reduced GNRs, they are still more highly conjugated than the oxidized starting material.

AFM imaging (Figure 4b) indicates the presence of long ribbons after the functionalization reactions. The f-GNR shown in Figure 4b is greater than 3 μm in length and is a single layer with an average height of ~1.2 nm. In general, the AFM-determined thickness of single-layer f-GNRs was measured to be 1.1−1.5 nm, which is slightly higher than that of reduced GNRs: 0.75−1.6 nm (for additional AFM images, see Supporting Information Figure S2). It is predicted that single-layer f-GNRs will have increased thickness due to the perpendicular covalent attachment of the functional group moieties.

SEM imaging (Figure 5) emphasizes the high aspect ratio ribbon structure of the f-GNRs. The typical length is 1−5 μm with widths from 80 to 320 nm. Figure 5a shows a single-layer folded nanoribbon that is over 2 μm in length and <200 nm wide. Longer few-layered ribbons such as those found in Figures 5c and 5d are representative of many that were imaged, with lengths >6 μm and widths ~300 nm.

The IR spectrum (Figure 6a) of oxidized GNRs shows a C—O stretch at ~1200 cm^{-1}, an O—H/COO—H stretch at 3600−2700 cm^{-1}, and a C=O stretch at 1720−1690 cm^{-1}. The spectrum of the reduced GNRs (Figure 6b), however, is devoid of any informative signal and resembles that of the MWCNT (graphite-like) starting material. Figure 6c shows the ATR-IR spectrum of f-GNRs **2c**. Asymmetric and symmetric stretches at 1520 and 1340 cm^{-1}, respectively, are attributed to the NO_2 group while the peak at 852 cm^{-1} can be assigned to the C—N bond. In addition, the aromatic stretch at 1586 cm^{-1} indicates the presence of nitrobenzene moieties on the f-GNRs.[33,34] The presence of NO_2 in **2c** and **3c** was also confirmed by XPS with a strong signal at 405 eV (Figure 2).

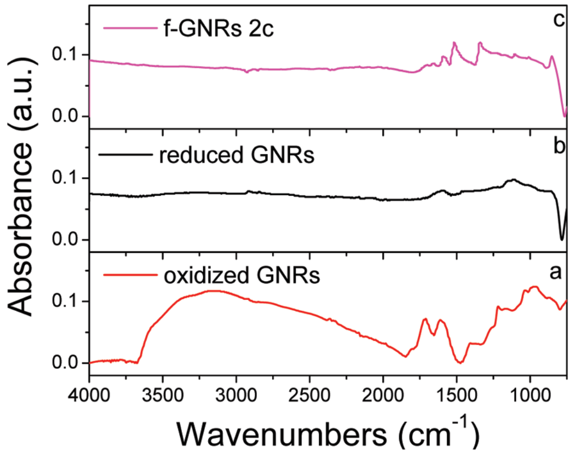

Figure 6. ATR-IR spectra of oxidized GNR starting material (a), reduced GNRs (b), and f-GNRs **2c** (c).

The Raman spectra of bulk f-GNRs and reduced GNRs using 633 nm laser excitation (Supporting Information Figure S3) show a profile similar to that of the oxidized starting material. The diamondoid (D) to graphitic (G) peak ratio is close to 2, confirming incomplete recovery of the graphene structure, similar to what was observed for functionalized graphene sheets.[21] The degree of functionalization was difficult to gauge using Raman spectroscopy. Edge defects may be responsible for the minimal change in the D/G ratios in graphene, and these should be even more pronounced in nanoribbons than in graphene sheets due to their high percentage of edge to basal plane content.[21]

The electrochemical properties of the f-GNRs prepared by route II were studied using CV. Oxidative and reductive cycles of **3** are shown in Figure 7. The onset potential can be determined from the intersection of two tangents drawn at the rising and background current of the CV. All f-GNRs exhibit oxidative response between 0.84 and 1.35 V (vs ferrocenium/ferrocene Fc^+/Fc), while the reductive response could not be observed even under an

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(33) Allongue, P.; Delamar, M.; Desbat, B.; Fagebaume, O.; Hitmi, R.; Pinson, J.; Saveant, J. M. *J. Am. Chem. Soc.* **1997**, *119*, 201–207.

(34) Delamar, M.; Hitmi, R.; Pinson, J.; Saveant, J. M. *J. Am. Chem. Soc.* **1992**, *114*, 5883–5884.

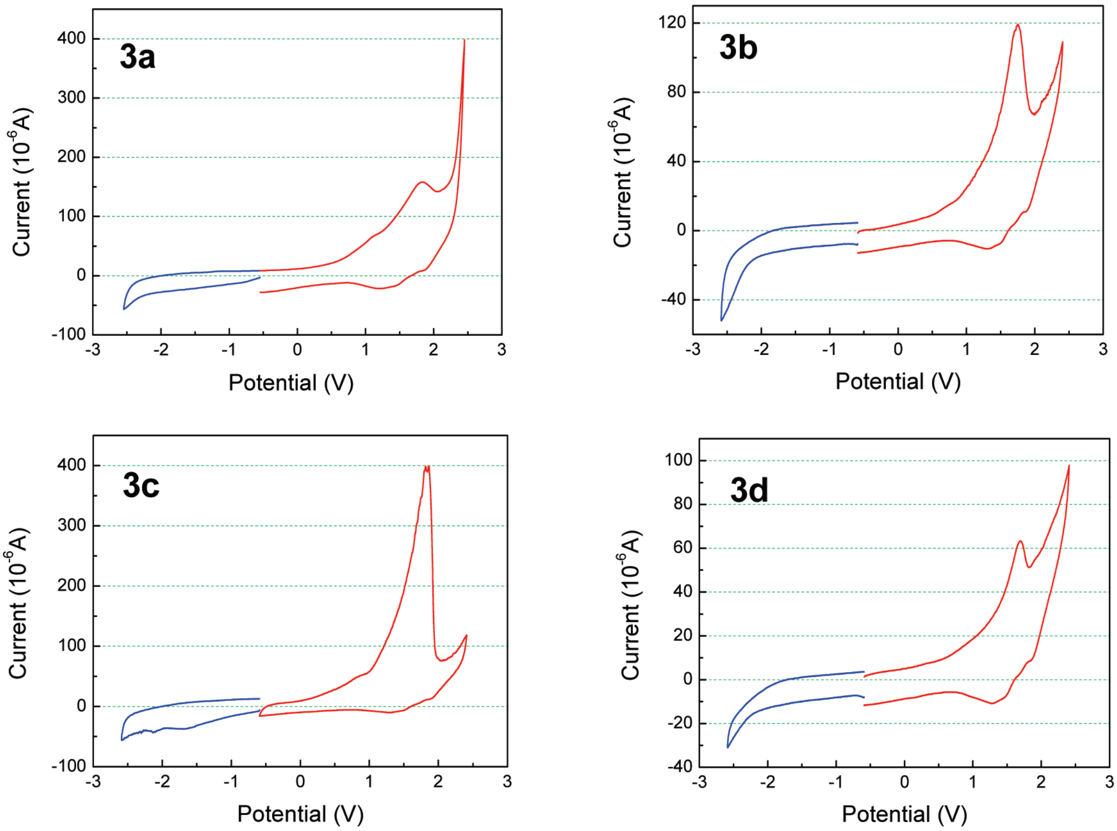

Figure 7. Cyclic voltammograms of f-GNRs **3a**−**3d**.

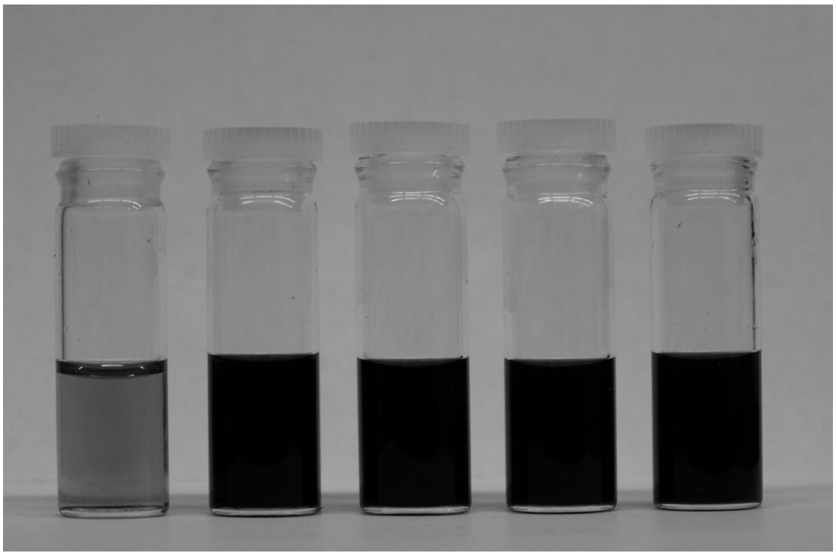

Figure 8. Supernatant remaining of postcentrifuged samples for solubility determination in DMF. From left to right, the samples are as follows: unfunctionalized control (reduced only), **2a**, **2b**, **2c**, **2d**.

air-free environment. This phenomenon is consistent with the reduced state of f-GNRs. The oxidized starting material shows reductive response, which is similar to graphite oxide.[35] The CV experiments confirm that the f-GNRs are in the reduced state.

The f-GNRs can be readily dispersed in DMF and NMP up to 1 mg/mL with minimal sedimentation. To further illustrate their respective solubilities in DMF, 3 mg f-GNRs was dispersed in 3 mL of DMF using an ultrasonic cleaner (Cole-Parmer model 08849-00) for 5 min followed by centrifugation in an Adams Analytical centrifuge (model CT 3201) for 15 min at 3200 rpm, after which a 2 mL aliquot of each supernatant was precipitated in acetone and filtered. The filter cake was then washed with acetone, dried, and weighed. The supernatant of f-GNRs gave dark solutions with some sedimentation (see images in Figure 8). The solubilities

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(35) Kotov, N. A.; Dekany, I.; Fendler, J. H. *Adv. Mater.* **1996**, *8*, 637–641.

of the f-GNRs are as follows: **2a**, 0.20 mg/mL; **2b**, 0.25 mg/mL; **2c**, 0.35 mg/mL; **2d**, 0.15 mg/mL; **3a**, 0.15 mg/mL; **3b**, 0.2 mg/mL; **3c**, 0.15 mg/mL; **3d**, 0.1 mg/mL.

Conclusion

Two convenient procedures were developed for the functionalization of graphene nanoribbons, allowing the nanoribbons to become soluble in organic solvents. One of the procedures successfully functionalized graphene using in situ generated diazonium salts, which broadens the possibilities of functionality since anilines can be used instead of preprepared diazonium salts. Due to their high aspect ratio and soluble properties, these ribbons might be useful materials for applications including composites, fibers, and thin film materials, and we are currently exploring those areas.

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Supporting Information Available: Fitting of XPS C1s spectra of **2d** and **3d**, additional AFM micrographs of f-GNRs, Raman spectra of all samples, and full author list for ref 11. This material is available free of charge via the Internet at http://pubs.acs.org.