Kinetics of Diazonium Functionalization of Chemically Converted Graphene Nanoribbons

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Graphene, a single atomic layer of sp[2] carbon atoms, has recently been the subject of intense research due to its unusual physical properties[1] and potential applications in electronics, sensors, composite materials, and other technological fields.[2] Since graphene is a possible material for the future electronics, it is important to have an ability to control its electrical properties *via* chemical doping. Previous works have demonstrated that gas molecules[3] and alkali metal atoms[4] can be physisorbed on the surface of graphene and thereby alter its conductivity, shift its neutrality point (V_{NP}), and differently affect the mobilities of the charge carriers. However, physisorption of the dopants can be problematic because the species are only weakly bound to graphene, and their continued presence on the surface may require delicate temperature and pressure control. Thus, the chemical modification of graphene, where functional groups are covalently bound to the surface, is a stable alternative that has yet to be fully studied. We disclose here a device embodiment to track the kinetics of covalent functionalization using the device current.

One approach to functionalization of various materials is diazonium chemistry.[5−11] Diazonium compounds with electron-donating or withdrawing groups have been used to modify the transport in silicon after aryl assembly on the device surfaces, resembling n- and p-dopants in their final behaviors.[12−14] Recently, experimental reports have appeared on diazonium grafting of graphene,[15−17] which could become a promising pathway toward graphene devices with modified electrical propeties[18] and graphene p−n junctions.[19] Here we report on the chemical functionalization of

ABSTRACT We demonstrate that graphene nanoribbons (GNRs) produced by the oxidative unzipping of carbon nanotubes can be chemically functionalized by diazonium salts. We show that functional groups form a thin layer on a GNR and modify its electrical properties. The kinetics of the functionalization can be monitored by probing the electrical properties of GNRs, either in vacuum after the grafting, or *in situ* in the solution. We derive a simple kinetics model that describes the change in the electrical properties of GNRs. The reaction of GNRs with 4-nitrobenzene diazonium tetrafluoroborate is reasonably fast, such that >60% of the maximum change in the electrical properties is observed after less than 5 min of grafting at room temperature.

graphene nanoribbons (GNRs), prepared by the chemical unzipping of carbon nanotubes (CNTs),[20−22] functionalized by 4-nitrobenzene diazonium tetrafluoroborate, with an emphasis on the electronic properties of the modified GNRs and the kinetics of molecular grafting.

RESULTS AND DISCUSSION

Grafting of the diazonium salt was performed on GNRs serving as the channels of the nanoscale electronic devices, as schematically shown in Figure 1a. This approach enables direct probing of the effect of chemical functionalization on the electronic properties of GNRs. Figure 1b shows a scanning electron microscopy (SEM) image of a typical electronic device based on a monolayer GNR. Only monolayer ribbons were selected by atomic force microscopy (AFM) for the device fabrication. The thicknesses of the annealed monolayer ribbons were typically in the range from 0.5 to 0.8 nm (Figure 1c).
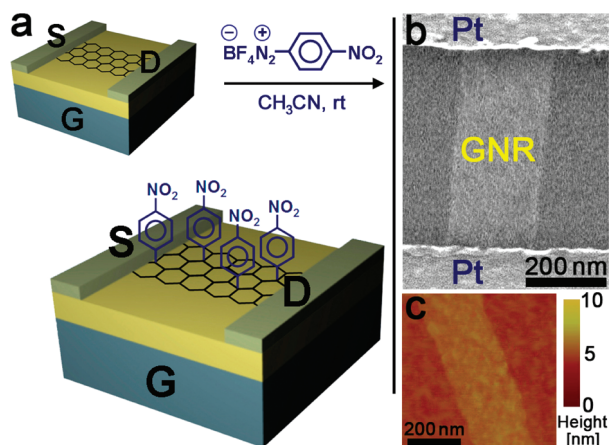
For the grafting experiments it was important to use the freshly synthesized diazonium salts due to the poor purity of commercially available diazonium salts and their gradual decomposition, no matter the

Figure 1. (a) Schematic of the chemical functionalization of GNR devices with 4-nitrophenyl groups. Electronic devices consisted of monolayer GNRs contacted with Pt source (S) and drain (D) electrodes. The devices were fabricated on a 200-nm-thick thermal SiO₂ over heavily doped p-type Si that was used as a back gate (G). (b) Top-view SEM image of a typical electronic device based on a single-layer GNR. (c) AFM image of a fragment of a typical monolayer GNR reduced by annealing at 900 °C in Ar/H₂ on the Si/SiO₂ substrate. This GNR has an average thickness ~0.7 nm.

purity, under ambient conditions. Therefore, 4-nitrobenzene diazonium tetrafluoroborate was synthesized and characterized by NMR just prior to grafting experiments; the details for the synthesis and the following graftings are given in the Experimental Section.

We used X-ray photoelectron spectroscopy (XPS) to verify that 4-nitrophenyl groups are strongly attached to GNRs. Figure 2 shows the N1s XPS spectra of the functionalized (*f*-) and control GNR samples. The samples for the XPS analyses were thick films of GNRs on Si/SiO₂ substrates, in contrast to individual GNRs used for the electrical measurements. No nitrogen was found in the control sample, suggesting that all of the nitrogen content of the *f*-GNRs was due to the treatment with diazonium salt, not from the solvent or air. Also no boron or fluorine signals were detected in the samples, eliminating the possibility of noncovalent phy-
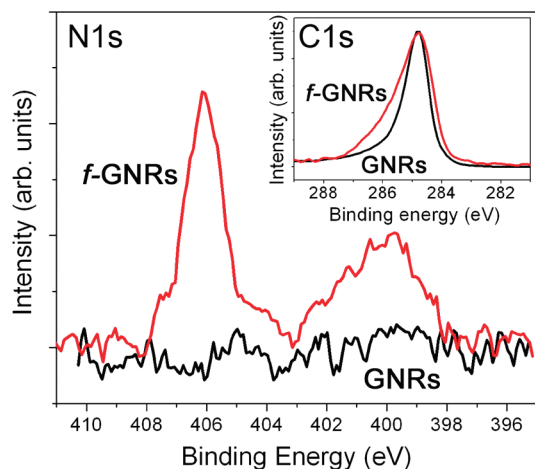
**Figure 2.** N1s and C1s XPS spectra of the functionalized (*f*-) and as-prepared GNRs.

sisorption of the molecules or the presence of residual BF₄⁻ counterions.

There are two peaks in the N1s XPS spectrum of *f*-GNRs (Figure 2). The sharp distinct peak at ~406 eV corresponds to the nitrogen in the nitro group. The broad peak at ~400 eV corresponds to nitrogen in the lower oxidation states. This peak was observed earlier in the study of epitaxial graphene grafted with 4-nitrophenyl groups and was explained by reduction of the nitro groups by X-ray radiation in the XPS spectrometer chamber.[16] A plausible alternative process could be *in situ* electrolytic reduction of the nitro groups by electrons from neighboring islands of intact graphene. Alternatively, the 400 eV peak could correspond to diazenyl groups introduced by electrophilic attack of the diazonium cation on aromatic rings (azo coupling reaction). Both N1s peaks were observed after extended washing (up to 72 h) of the *f*-GNRs with CH₃CN, and even after drying the samples in vacuum at 200 °C, suggesting the strong attachment of 4-nitrophenyl groups to the GNRs.

The peak in the C1s XPS spectrum (see the inset in Figure 2) broadens after the grafting. This effect could be attributed to two different factors: (1) the presence of 4-nitrophenyl groups with C—N bonds in the *f*-GNR sample, which results in the appearance of a new component at 285.7 eV and thus broadening of the main C peak at 284.8 eV toward the higher energy region; (2) an increase in the number and contribution of graphene-derived sp³ C bonds.

Figure 3 illustrates the effect of grafting on the electrical properties of GNRs. Figure 3a shows that as-prepared GNR devices exhibited electric field effects, and the ambipolar transfer characteristics for the same device are shown in Figure 3b. Interestingly, after the diazonium treatment, the conductivity of GNR devices gradually decreases with grafting time over the entire V_g-range, which can be explained by the covalent attachment of 4-nitrophenyl groups to the GNRs, resulting in the transition of the graphene carbon atoms from sp² to sp³ hybridization. This result contrasts with the data reported for graphene devices treated with 4-bromobenzene diazonium salt, where the current at the neutrality point (I_{NP}) did not change after grafting.[18] However, in this case no significant shift of V_{NP} or other prominent doping effects were observed as were reported in ref 18. These results might suggest that functionalization with different aryl diazonium salts could produce GNRs with differing electrical properties; changing the group in the para position of the phenyl group could modulate doping-like effects. This could be promising for tuning electronic properties of graphene devices through chemical functionalization.

Since functionalization of GNRs results in a decrease in their conductivity, we can monitor the kinetics of the reaction by probing the electrical properties. The black squares in Figure 3c show the current at the neutrality
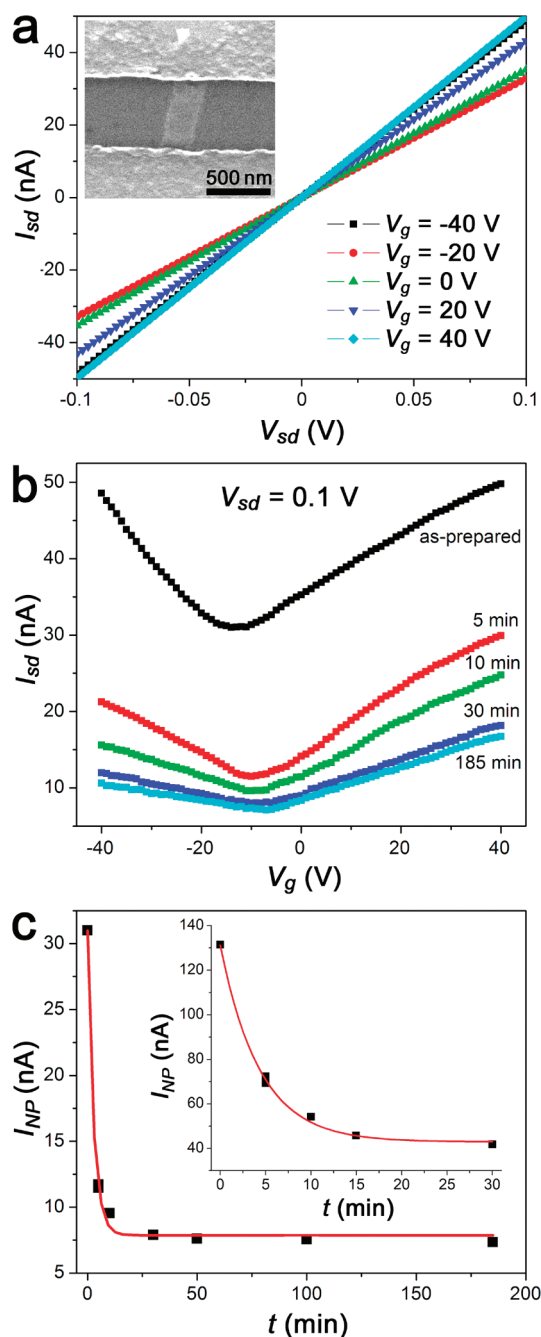
Figure 3. (a) $I_{sd} - V_{sd}$ curves recorded at different gate voltages for the GNR device shown in the SEM image in the inset. (b) $I_{sd}-V_g$ curves recorded at $V_{sd} = 0.1$ V for the same electronic device in panel a after several consecutive grafting experiments; the captions show the total grafting time. (c) Dependence of the minimum current (I_{NP}) at the neutrality point versus grafting time for the same electronic device. Black squares show experimental data points taken from panel b and the red line is their fitting with the eq 3; see text for details. The inset shows a fragment of a similar dependence for another GNR device. All IV measurements were performed in a probe station at $\sim 10^{-5}$ Torr.

point (I_{NP}) versus grafting time (t) for two of the measured devices. The reaction is reasonably fast, as I_{NP} drops $\sim$2-fold within the first 5 min of reaction. To simulate the data, a simple kinetics model can be derived by making two assumptions:

(1) Each 4-nitrophneyl group attached to the GNR results in a transition of one carbon atom from sp^2 to sp^3 hybridization and a corresponding decrease in the conductivity of the GNR:

$$\Delta I(N) \approx -N \qquad (1)$$

where I is the current through the ribbon at a certain bias and N is the number of 4-nitrophenyl groups already attached to the GNR.

(2) The more 4-nitrophenyl groups attached to the GNR, the slower the reaction rate becomes since the number of the sites available to 4-nitrophenyl groups decreases. So, we can assume that

$$\frac{dN}{dt} \approx -N \qquad (2)$$

With a combination of eqs 1 and 2 and application of the boundary conditions, an equation for the current through the GNR versus the grafting time can be derived:

$$I(t) = (I_0 - \Delta I_{max}) + \Delta I_{max} \exp(-t/t') \qquad (3)$$

where I_0 is the current before grafting, ΔI_{max} is the maximum current drop after attachment of the maximum number of 4-nitrophenyl groups possible, and t' is the characteristic time of reaction when the current drop is $(e-1)/e\Delta I_{max} \approx 0.63\Delta I_{max}$.

The experimental data for all 10 devices tested can be described by eq 3; two examples are shown in Figure 3c (red lines). The characteristic time of the reaction (t') ranges from 3 to 4.5 min, again showing that functionalization occurs reasonably quickly.

The difference between the values of t' measured for different devices suggests that ribbons may have different reactivities. This may be partially explained by the fact that the reduced graphene oxide, which is obtained through the similar oxidation−reduction process as GNRs, has a domain structure that comprises nearly perfect nm-sized graphene areas interspersed with defect areas.[23] It is likely that GNRs have similar domain structure, which would be in a good agreement with the previously reported results of the temperature-dependent electronic transport measurements.[21] In this case, the electronic properties and reactivity of each GNR should depend on the distribution and the relative position of the domains within the ribbon, which could explain the observed variation in t' for different devices. The rate of reaction of 4-nitrobenzene diazonium tetrafluoroborate with the GNR depends on the relative positions of the 4-nitrophenyl groups already attached to the ribbon, and this steric factor could be another reason for the deviations of the experimental data from the simple model eq 3; these steric effects should become more significant with increased reaction time.
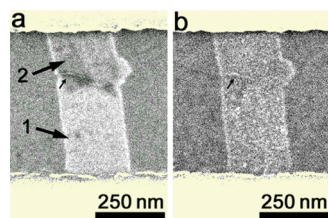
Figure 4. SEM images of the same GNR device (a) before and (b) after diazonium functionalization for 1 h. (a) Shown is a monolayer GNR that spans from one Pt electrode to another one; a part of GNR is covered by another ribbon; the numbers indicate monolayer and bilayer regions. (b) After the grafting the brightness difference between these regions is less distinct. The small arrows in panels a and b show a wrinkle formed by the top ribbon.

Figure 5. Time dependence of current $I = I_{GNR} - I_{ref}$, where I_{GNR} and I_{ref} are the currents through the GNR and reference devices, respectively, which were simultaneously measured in a two-terminal geometry at $V = 0.1$ V. From $t = 0$, both devices were immersed in the same CH_3CN solution of 4-nitrobenzene diazonium tetrafluoroborate. The scheme of the experiment is displayed in the upper inset but the reference device measured using the same electrical circuit is not shown. The lower inset shows that once immersed in a solution, the GNR device can be presented as the parallel connection of R_{dev} and R_{sol}, where R_{dev} is the actual resistance of the GNR device and R_{sol} corresponds to the resistance of the solution.

To further investigate the diazonium functionalization of GNRs, SEM images of the electronic devices were compared before and after grafting. In all but one case, a single-layer GNR spanned the entire distance between the two electrodes. In one case, which accentuates the grafting effects, we show in Figure 4 a GNR that comprises the coexistence of monolayer and bilayer parts. Monolayer and bilayer ribbons on Si/SiO$_2$ can be distinguished by the relative brightness in SEM images: bilayer ribbons are darker than the monolayer ribbons, which was correlated with AFM measurements.[22] Interestingly, this brightness difference becomes far less distinct after the grafting and can be hardly seen even at very high contrast as in Figure 4b, since after the grafting both monolayer and bilayer parts are covered by the same thin layer of functional groups. Only a distinctive wrinkle formed by the top ribbon can be distinguished through the organic layer, thus indicating that the top ribbon is still present.

In the described experiment it took about 2−3 days (including grafting, evacuation in the probe station, and electrical measurements) to obtain each data point. Alternatively, we have investigated the kinetics of the functionalization of GNRs *in situ*, as schematically shown in the upper inset in Figure 5. Gold wires were attached to the Pt electrodes by indium soldering, and then they were connected to an Agilent 4155C semiconductor parameter analyzer. The advantages of this experimental design are (a) the high resolution of the resulting kinetic curves (~1 data point/s was measured) and (b) the minimized impact of atmospheric adsorbates. However, gating could not be applied since the CH_3CN solution of 4-nitrobenzene diazonium salt is slightly conductive.

Once the device is immersed in the solution, the measured current increases since the resistances of the GNR device (R_{dev}) and the solution (R_{sol}) are in parallel, as shown in the lower inset in Figure 5. Therefore, in this experiment we simultaneously measured a GNR device and a reference device immer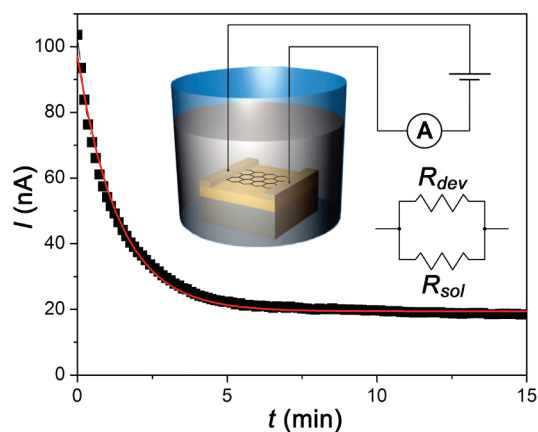sed in the same solution, where the reference device was exactly the same as a GNR device but without a nanoribbon. Figure 5 shows the current I, that was calculated as $I = I_{GNR} - I_{ref}$, where I_{GNR} and I_{ref} are the currents through the GNR and reference devices, respectively, which were simultaneously measured, each in a two-terminal geometry at $V = 0.1$ V. Figure 5 shows that immediately after devices are immersed in the CH_3CN solution of 4-nitrobenzene diazonium salt, the current I starts decreasing due to the chemical functionalization of a GNR and the corresponding increase in R_{dev}. The resulting kinetics curve measured in a solution resembles those recorded in vacuum and can also be fitted by eq 3. This curve corresponds very well to those obtained in Figure 3c, but the *in situ* method provides far more precision.

In summary, we have demonstrated that GNRs can be chemically functionalized by diazonium salts while the kinetics of the functionalization can be monitored by probing the electrical properties of GNRs, either in vacuum after the grafting, or *in situ* in the solution. The change in the electrical properties of GNRs can be described by a simple kinetics model. The reaction of GNRs with 4-nitrobenzene diazonium tetrafluoroborate is reasonably fast, such that >60% of the maximum change in the electrical properties is observed after less than 5 min of grafting at room temperature. Overall, diazonium functionalization could be a promising way to alter the electrical properties of graphene devices. The stability of GNR devices in a solution also enables their possible use in electrochemical applications.

EXPERIMENTAL SECTION

Fabrication of GNR Devices. Electronic devices were fabricated as described in our previous work.[21] Briefly, multiwalled CNTs from Mitsui & Co. (lot no. 05072001K28) were first unzipped to graphene oxide nanoribbons (GONRs) in 0.5 wt %/vol solution of $KMnO_4$ in H_2SO_4 so that 5 g of $KMnO_4$ was used for each 1 g of MWCNTs.[20] The resulting GONRs were reduced by hydrazine at 95 °C to chemically converted GNRs that were subsequently dispersed over a Si/SiO_2 substrate (heavily doped p-type Si with a 200-nm-thick thermal SiO_2 layer) and annealed in H_2/Ar (1:1, < 1 atm) at 900 °C for 1 h. The GNRs on the substrates were studied by SEM (JEOL-6500 field-emission scanning electron microscope). Only monolayer GNRs were selected for the fabrication of electronic devices; the single-layer thicknesses of those ribbons were confirmed by AFM (Digital Instruments Nanoscope IIIa). Pt contacts (20 nm thick) were patterned across the ribbons by standard electron beam lithography followed by electron beam evaporation. Figure 1b shows an SEM image of a typical electronic device. Overall, 10 devices were fabricated for this study; the widths of the GNRs were 200−350 nm and the electrode spacings were 500−800 nm. Previous studies of similar devices revealed that GNRs have an average conductivity of 35 S/cm and exhibit ambipolar electric field effects, and with the Pt electrodes, contact resistances are minimal as the 2- and 4-probe measurements are nearly identical.[21]

Synthesis of 4-Nitrobenzene Diazonium Tetrafluoroborate. CH_3CN (Sigma-Aldrich, 99.8%, anhydrous) and 4-nitroaniline (≥99%, Sigma-Aldrich) were used as received. $NOBF_4$ was synthesized as previously described.[24,25] An oven-dried round-bottom flask was brought into a N_2 glovebox and charged with 2.54 g (21.9 mmol) of $NOBF_4$, sealed with a septum, and then removed from the glovebox. The flask was placed under an Ar atmosphere, and the solid was then dissolved in 60 mL of CH_3CN, after which the flask was cooled to 0 °C in an ice bath. A second round-bottom flask was charged with 3.00 g (21.7 mmol) of 4-nitroaniline, sealed with a septum, evacuated, and refilled with Ar (3×), and then 40 mL of CH_3CN was added. The contents of the second flask were then slowly transferred by cannula into the first. After 30 min, Et_2O was added to the flask to precipitate the resulting diazonium salt. The precipitate was filtered and washed thoroughly with cold Et_2O to yield 4.44 g (18.7 mmol, 86%) of a light-yellow solid. The solid was carefully stored in the dark at −10 °C under Ar before and after each use to avoid decomposition. ^1H NMR (400 MHz, D_2O): δ 8.92 (d, J = 9.2, 2H), 8.76 (d, J = 9.2, 2H). ^{13}C (100 MHz, D_2O): δ 154.2, 134.4, 126.8, 120.74.

Diazonium Functionalization of GNR Devices. In the grafting experiments, the substrates bearing the GNR devices were brought into a N_2 glovebox and placed in a fresh 10 mL solution of the diazonium salt in Ar degassed CH_3CN (1 mg/mL). After remaining in the solution for the required amount of time (from several min to a few h), the substrates were thoroughly rinsed with CH_3CN (3×), blown dry with N_2, and further dried under vacuum in the glovebox antichamber. The samples were transported to and from the probe station (Desert Cryogenics TT-probe 6 system) under an inert atmosphere to minimize exposure to oxygen and humidity. After the samples were loaded in the probe station, they were kept under vacuum ($\sim10^{-5}$ Torr) for 2−3 d to minimize the effect of the molecules adsorbed on the surface of GNRs. During this evacuation period we measured the electronic properties of the GNR devices every 12 h until the p-doping effect of the molecular adsorbates disappeared and the electronic behavior of the devices stabilized. The electrical measurements were performed at room temperature (rt) using an Agilent 4155C semiconductor parameter analyzer, and then the devices were transported back to the glovebox for the next grafting. Several consecutive grafting−evacuation−measurement cycles were made until the grafting did not result in apparent changes in the electrical properties of the GNRs.

XPS Analyses. XPS spectra were recorded using a PHI Quantera SXM scanning X-ray microprobe. Bulk GNR samples (thick films of GNRs on Si/SiO_2 substrates) were treated with a CH_3CN solution of diazonium salt for 15 min, as described above, then washed for 30 min in CH_3CN and then in acetone for 10 min to remove possible traces of CH_3CN. The control sample was prepared by immersing similarly thick GNR films in CH_3CN for 45 min and then washing in acetone as described above.

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