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Tuning of n- and p-Type Reduced Graphene Oxide Transistors with the Same Molecular Backbone

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As silicon integrated circuits approach their theoretical limits, many researchers have turned to non-silicon-based materials in the hope of discovering new materials upon which the next generation of electronic devices will be based.[1] Carbon nanomaterials are promising alternative candidates to replace silicon in device technologies.[2] Recently, graphene has been widely investigated for its field-effect properties, and transistors composed of the material have been used in some applications.[3] Graphene is a mono-layer of graphite in which a carbon backbone forms a two-dimensional (2D) hexagonal structure as a zero-gap semiconductor. Field-effect transistors (FETs) using graphene as a channel between the source and drain suffer from the absence of a bandgap.[4] To open and tune an energy gap in graphene, various approaches have been developed to improve the semiconducting properties, such as those involving quantum dots,[5] nanoribbons,[6] nanomeshes,[7] and graphene binding to particular substrates.[8]

Chemical doping is one such subject that draws attention. The type and concentration of electron or hole carriers in graphene can be controlled by the introduction of metals or molecules onto the graphene surface. Several chemical species are known to produce doping effects in mechanically exfoliated graphene. n-Type graphene FETs doped with electron-donating materials have been observed when graphene FETs have been exposed to titanium and potassium with charged impurity scattering,[9a] TiO2,[9b] NH3[10] and CO vapors[10a] or small molecules (polyethyleneimine)[11] or small molecules (1,5-naphthalenediamine and 9,10-dimethylanthracene).[12] Alternatively, p-type graphene FETs doped with electron-withdrawing materials have been observed when graphene FETs have been exposed to H2O and NO2 vapors[10a] or small molecules (4-bromobenzenediazonium tetrafluoroborate,[11] tetrasodium 1,3,6,8-pyrenetetrasylfonic acid, and 9,10-dibromoanthracene).[12] Thus, to realize the p- and n-doping effects of graphene FETs, the introduction of functionalized molecules that have electron-withdrawing or -donating properties is necessary. Until now, however, there is still no clear understanding of the molecular-doping effect, even though various functionalized molecules have been tested for p- and n-type graphene FETs.

The main reason for the unclear doping effect of the molecules is that the previous molecules selected for p- or n-type had different backbones, leading to limited understanding of the origin of the molecular-doping effect. For a clear demonstration of this effect, it is necessary for the doped molecules to have the same molecular backbone and to possess a series of functional groups. In addition, semiconducting channels in graphene layers have been prepared by means of several different methods. A simple and easy method is based on the creation of colloidal suspensions through the use of a graphene oxide (GO) precursor to achieve individual layers. GO is easily exfoliated and well dispersed in water, allowing simple spin-coating onto any substrate. Field-effect devices fabricated through the spin-casting of GO layers, followed by reduction into reduced graphene oxide (rGO) typically exhibit semiconducting behavior with low conductivity.[13] We choose the pyrene molecule backbone for several reasons. First, pyrene derivatives could stably bind to the rGO channel through strong π–π interactions between their aromatic rings and the graphene. These π-electron-rich pyrene derivatives were reported as a stable biosensor[14] and also as intercalated molecules for the dispersion of graphene.[15] Second, we could attach withdrawing or donating groups to the pyrene moiety with a simple reaction and easy purification.[16]

In the present work, rGO FETs with few layers of rGOS were successfully prepared as a semiconducting channel through the reduction of GO and modification with pyrene derivatives including 1-aminopyrene (Py-NH2), 1-nitropyrene (Py-NO2), 1-pyrenecarboxylic acid (Py-CO2H), and 1-pyrenesulfonic acid (Py-SO3H) (Figure 1). The π-electron-rich pyrene backbone was designed for immobilization on the π-electron-rich rGO channel through

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Figure 1. Chemical structure of the pyrene molecules used as dopants.
noncovalent π–π interactions between the pyrene moiety and graphene. To the best of our knowledge, this is the first reported observation of p- and n-doped graphene FETs using the same molecular backbone functionalized with electron-donating and -withdrawing groups. These pyrene derivatives could stably bind to the rGO channel through strong π–π interactions between their aromatic rings and the graphenes. The electrical measurements on rGO-based FETs suggest that the pyrene molecules with electron-donating groups cause n-doping (increasing electron density) on the rGO, while those with electron-withdrawing groups impose p-doping (reducing electron density). To electrically examine the doping effects of the pyrene derivatives, we successfully fabricated bottom-gated FETs using rGOs, which were prepared through the reduction of GO using vapor hydrazine (Figure 2a–2c). Thermal annealing was performed to obtain a better contact. Surface characterization of the rGO on the devices was characterized by field emission scanning electron microscopy (FESEM) and atomic force microscopy (AFM). Typical low-magnification FESEM images of the electrode with deposited rGO recorded at magnifications of ×1500 and ×10000 are shown in Figures S1a and S1b, respectively in the Supporting Information. These images revealed the rGO channel, bridging the source and drain electrodes, behaved as the semiconducting channel. The channel length and width were approximately 10 and 50 μm, respectively.

Figure S2 in the Supporting Information shows a tapping-mode AFM image and line scan of rGO on FET device. The cross-sectional analysis gave a sheet thickness of around 1.5 nm, which confirmed a few layers of rGO. For the immobilization of pyrene molecules onto noncovalent, functionalized rGO, the rGO FET devices were dipped in a solution of pyrene (10 mM of pyrene in DMF) for 12 h at room temperature under an inert atmosphere. The resulting samples were rinsed three times in pure DMF to wash away excess pyrene derivatives. Pyrene molecules immobilized on the rGO channel were characterized by using Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). The functionalization efficiency of pyrene molecules was verified by XPS (Figure S3 in the Supporting Information). The XPS of bare rGO contains no nitrogen, but the percentage of nitrogen after doping pyrene was estimated to be about 4%. It is believed that the pyrene molecules were covered onto the rGO channel. Figure S4 in the Supporting Information shows the C1s, N1s, and S2p regions pertaining to the XPS spectra of the pyrene molecules immobilized on the rGO channel. A key feature of the XPS data is the two N1s peaks of Py-NO2 at 400 and 406 eV, as shown in Figure S4c in the Supporting Information. The peak of the higher binding energy near 406 eV can be attributed to a NO2 functional group, while that of the lower binding energy at approximately 400 eV was assigned to the N1s of the NH2 functional group, created through the reduction of NO2 under the X-ray beam during the XPS experiment, as previously reported. After 50 scans, the N1s peak of the NO2 functional group at 406 eV was entirely changed into the N1s peak of the NH2 functional group at 400 eV. To avoid weakening of the photon beam, the number of scans for collecting the N1s signals was limited to five.

Figure 3 showed the Raman spectra for rGO and rGO modified with pyrene molecules, for which the D, G, and 2D bands were assigned and summarized in Table 1. In particular, the D (1344), G (1580), and 2D (2679 cm−1) bands are useful for understanding the effects of electron- and hole-doping. The G and 2D band frequencies are slightly upshifted after the introduction of pyrene molecules. The D band position is insensitive to the interaction with n- and p-doping materials, but the D band intensity decreased in comparison to that of the G band, as was oppositely observed in a previous study. Alternatively, the 2D band showed an increase in frequency and a decrease in intensity, indicating that the defects in the rGO channel were repaired with the immobilization of the pyrene derivatives. The information was characterized by field emission scanning electron microscopy (FESEM) and atomic force microscopy (AFM). Typical low-magnification FESEM images of the electrode with deposited rGO recorded at magnifications of ×1500 and ×10000 are shown in Figures S1a and S1b, respectively in the Supporting Information. These images revealed the rGO channel, bridging the source and drain electrodes, behaved as the semiconducting channel. The channel length and width were approximately 10 and 50 μm, respectively.

Table 1. Raman shifts in the G and 2D frequencies of pyrene derivatives.

<table>
<thead>
<tr>
<th>Frequency (cm⁻¹)</th>
<th>RGO</th>
<th>Py-NH2</th>
<th>Py-NO2</th>
<th>Py-CO₂H</th>
<th>Py-SO₃H</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>1344</td>
<td>1351</td>
<td>1349</td>
<td>1350</td>
<td>1351</td>
</tr>
<tr>
<td>G</td>
<td>1580</td>
<td>1598</td>
<td>1605</td>
<td>1598</td>
<td>1601</td>
</tr>
<tr>
<td>2D</td>
<td>2679</td>
<td>2692</td>
<td>2693</td>
<td>2686</td>
<td></td>
</tr>
</tbody>
</table>

[a] Not detected.
tensity of the 2D band decreases with an increase in the degree of dopant, and the 2D band doped with Py-NH₂ (i.e., pyrene with an electron-donating group) was not observed in the Raman spectrum of rGO.

The ratio of the intensities of $I(2D)/I(G)$ and $I(D)/I(G)$ of rGOs doped with pyrene derivatives are considered to be sensitive to doping. In Raman spectra after being doped with pyrene functional derivatives, both pyrene electron-donating and electron-withdrawing groups (Figure 3b–3e) cause a decrease in the intensity ratios of $I(2D)/I(G)$ and $I(D)/I(G)$, compared with that of bare rGO (Figure 3a). Interestingly, the intensity ratio of $I(D)/I(G)$ of rGOs doped with pyrene functional molecules is opposite to that observed with $I(D)/I(G)$ of rGOs doped with benzene functional molecules reported previously. It is demonstrated that the rGOs doped with pyrene derivatives show a high sensitivity to a molecular-doping effect through an analysis of Raman spectra, promising to provide p- and n-type devises.

The rGO FET in an air atmosphere typically shows a p-type behavior that is caused by moisture, oxygen, and/or defects introduced onto the rGO during device fabrication. To avoid these unwanted effects on the rGO channel, annealing of the rGO FET at 200°C under vacuum was performed until a stable neutrality point (minimum conductance point, $V_{NP}$) remained unchanged. Figure 4 showed the transfer characteristics of the drain current ($I_d$) versus back-gate voltage ($V_g$) for the rGO FET before and after doping with pyrene derivatives. For Py-NH₂ (Figure 4a) the neutrality point was negatively shifted by $-29.5$ V, from $-2.1$ to $-31.6$ V, indicating that the Py-NH₂ molecule induced n-doping that increased the electron concentration on the rGO channel.

In a parallel study, the results of which are presented in Figure 4b–4d, transfer curves were measured before and after doping with Py-NO₂, Py-CO₂H and Py-SO₃H, respectively. The shifts in the $V_{NP}$ of rGO FET caused by the four different pyrene molecules are summarized in Table 2.

Amazingly, pyrene derivatives functionalized with electron-withdrawing groups (i.e., Py-NO₂, Py-CO₂H, and Py-SO₃H) exhibited a p-doping effect, as shown in Figure 4b–4d, respectively, while a pyrene molecule functionalized with an electron-donating group (i.e., Py-NH₂) revealed n-doping, as depicted in Figure 4a. The most electron-withdrawing group, Py-NO₂, produced the largest positive shift in $V_{NP}$ in comparison with those of Py-CO₂H and Py-SO₃H, resulting in the greatest p-doping effect. As shown in Figure S5 in the Supporting Information, the neutrality point voltage shifts ($\Delta V_{NP}$) obtained by the functionalized pyrene doping on the rGO FET devices and the Hammett values ($\sigma_p$) of the functionalized pyrene derivatives were almost linearly correlated with a positive slope. For a control experiment, pyrene with no electron-withdrawing or -donating groups provided no doping effect, but increased the electrical conductivity, as demonstrated in Figure S6 in the Supporting Information. Owing to its semiconductor-like nature, rGO can be doped under appropriate conditions, leading to

![Figure 4. Drain current/gate-voltage curves for the molecular doping effect on the rGO FET devices before (solid line) and after doping (dashed or thin line) with a) Py-NH₂, b) Py-NO₂, c) Py-CO₂H, and d) Py-SO₃H.](image)

<table>
<thead>
<tr>
<th>Doping</th>
<th>Py-NH₂</th>
<th>Py-NO₂</th>
<th>Py-CO₂H</th>
<th>Py-SO₃H</th>
</tr>
</thead>
<tbody>
<tr>
<td>before</td>
<td>$-2.1$</td>
<td>$-7.3$</td>
<td>$-9.1$</td>
<td>$-12.1$</td>
</tr>
<tr>
<td>after</td>
<td>$-31.6$</td>
<td>$+5.7$</td>
<td>$+0.2$</td>
<td>$-5.2$</td>
</tr>
</tbody>
</table>

[a] These values showed the average of several devices.
a higher conductivity.\textsuperscript{[30]} Thus, the immobilized pyrene molecules on the rGO channel healed defects of the rGO channel, leading to improvement in conductivity. As a result, we clearly demonstrated the origin of the molecular-doping effect for molecules with the same pyrene backbone that possess electron-withdrawing and -donating groups immobilized onto the rGO FET.

Normalizing the $I_d$-$V_g$ curves with respect to $V_{NP}$ revealed a distinct asymmetry in electron and hole conductance (Figure 5). Py-NO$_2$ exposure did not significantly affect hole conduction ($V_g < V_{NP}$), but there was a clear suppression of the electron conduction ($V_g > V_{NP}$; Figure 5b). Also Py-CO$_2$H and Py-SO$_3$H gave similar results (Figure S7 in the Supporting Information). This phenomenon is a type of doping-induced conductance asymmetry, in which conductance of only one carrier type is suppressed. Alternatively, the other type of doping asymmetry exhibited after Py-NH$_2$ treatment had the opposite effect to that observed. After Py-NH$_2$ treatment, the hole conductance ($V_g < V_{NP}$) was preserved or slightly suppressed,\textsuperscript{[31]} while the electron conductance ($V_g > V_{NP}$) was sharply increased (Figure 5a). The asymmetric doping-type depends on the functionalized electron-withdrawing or -donating group. Specifically, the charge type of the dopant determined the type of asymmetry, for which the electron conductance with electron-withdrawing groups (e.g., Py-NO$_2$ and Py-CO$_2$H) was suppressed, while that with the electron-donating group (e.g., Py-NH$_2$) was increased.

In summary, rGO FETs consisting of a few layers of rGOS used as a semiconducting channel were successfully prepared through the reduction of GOs connected between two electrodes. A pyrene backbone with a series of functional groups, including electron-donating (Py-NH$_2$) and - withdrawing groups (Py-NO$_2$, Py-CO$_2$H, and Py-SO$_3$H), were used. Using a simple dipping method, the pyrene derivatives were stably immobilized on the semiconducting rGO channel, confirmed by Raman spectroscopy, XPS and $I$–$V$ characteristic measurements. Raman spectroscopy illustrated that the D band position was insensitive to the interaction with n- and p-doping materials, but the band intensity decreased compared to that of the G band. The intensity ratios of the $I(D)/I(G)$ and $I(D)/I(G)$ were sensitive to the molecular-doping effect. The pyrene backbone with electron-withdrawing (i.e., Py-NO$_2$, Py-CO$_2$H and Py-SO$_3$H) and -donating groups (i.e., Py-NH$_2$) showed p- and n-doping effects, respectively, while the pyrene backbone with no electron-withdrawing or -donating groups showed no doping effect, demonstrating that the origin of molecular doping was based on the functional groups. In addition, the doping of the rGO channel with any pyrene molecules provided a slightly higher conductivity. It is assumed the immobilized pyrene molecules healed defects of the rGO channel. This research to clearly understand the origin of the molecular doping effect on a graphene-based semiconducting channel provides new insight into the design of a complete circuit of p- and n-type graphene transistors.

**Experimental Section**

Materials and characterization: Air- and moisture-sensitive reactions were performed under a dry nitrogen atmosphere using standard Schlenk techniques. Organic solvents were freshly distilled from appropriate drying reagents prior to use, if necessary. 1-Pyrenesulfonic acid, 1-pyrene-carboxylic acid and other starting materials were purchased from Aldrich and were used without further purification. $^1$H and $^{13}$C NMR spectra were recorded on a VG Quattro mass spectrometer using the electron ionization mode. 1-Nitropyrene\textsuperscript{[16a]} and 1-aminopyrene\textsuperscript{[18]} were synthesized by using modified literature methods. GO was prepared from natural graphite powder (Bay Carbon, SP-1 graphite) by using a modified Hummers method.\textsuperscript{[19–21]} Raman spectroscopy (Reinshaw, RM1000-InVia) and XPS (VG microtech ESCA 2000) were used for surface characterization. A 4200 Keithley semiconductor characterization system was used for measurements of the electrical properties of the device.

Preparation of the GO solution: GO (50 mg) and deionized (DI) water (100 mL) were mixed together in a centrifuge-tube. To dispersion of GO in the DI water, sonication for more than 2 h (using a Branson ultrasonicator) was necessary for complete dispersion of GO. The resulting GO solution was shaken at 200 rpm for 1 h, centrifuged at 500 rpm for 1.5 h, and then left standing for 2 h. The clear supernatant was collected for further experimental.

Fabrication of FET device using rGO: An electrode-fabricated device was chemically cleaned using a piranha solution (98% H$_2$SO$_4$/30% H$_2$O$_2$ = 3:1 v/v) for 5 min. The device was followed by washing several times with DI water and ethanol and a final drying under a stream of nitrogen gas.
Reduced Graphene Oxide Transistors

The clear GO solution was collected at a volume of 100 μL in a micro-syringe and then dropped cast onto the device spinning at 4000 rpm for 30 s. The devices were dried for more than 24 h under vacuum condition. The reduction of the GO films was performed using 98% hydrazine vapor generated in a closed cell maintained at 90°C overnight. This was followed by several washes with DI water and ethanol and then a drying step under a stream of nitrogen gas. Finally, the rGO devices were dried for more than 24 h under vacuum, and then thermal annealing was performed at 200°C to obtain a better contact.

Immobilization of pyrene molecules on the rGO device: To noncovalently functionalize rGO, the pyrene molecules were dissolved in DMF. These solutions (10 μM) were then carefully immobilized on the surface of the rGO film for 12 h in a glove box. The sample was rinsed three times in pure DMF to wash away excess pyrene derivatives and dried. Electrical characteristics of the rGO-transistors were measured in a vacuum with a Keithley 4200 semiconductor characterization system unit.

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