Fabrication and Evaluation of Solution-Processed Reduced Graphene Oxide Electrodes for p- and n-Channel Bottom-Contact Organic Thin-Film Transistors

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Organic thin-film field-effect transistors (OTFTs) switch and modulate current using a thin-film of an organic compound as the active electronic material.1,2 This organic component makes them attractive in a range of high-value applications that are complementary to those of silicon-based electronics.3–5 Such applications involve situations requiring low weight, flexibility, transparency, conformal coverage of nonplanar and complex surfaces, large format, low cost per area, chemical and biological sensing, etc.6–9 Many factors can intervene to shape the end performance of OTFTs including the purity of the organic semiconductor, the thin-film processing, the choice of gate dielectrics and of electrical contacts, etc.5,10–12 The richness of such phase-space makes OTFT research both challenging and exciting as the foreseen applications come closer to reality. In this work we focus on the fabrication and performance of graphene-oxide-based electrical contacts for OTFTs.

Reduced graphene oxide (RGO) comprises a class of nanometer-scale materials resulting from the sequential oxidation and reduction of graphene.13,14 Graphene is a two-dimensional semimetallic nanocarbon allotrope with physical properties relevant to applications from mechanical reinforcement to transparent electrical conductors and the study of quantum phenomena.14–17 Graphene is difficult to process on a large scale since the material is insoluble and does not sublime. Thermal desorption of Si from SiC15,18 and, recently, vapor-deposition methods19,20 are common approaches to fabrication of graphene films. In contrast, graphene oxide (GO) can be deposited from water suspensions,13,21 and solution-processed GO has been used to form stand-alone films,22 prepare composites15,16 and obtain large-scale films.23,24 Importantly, GO films are electrically insulating25,26 but can be reduced through chemical reduction,27 hydrogen plasma,28 or thermal desorption of oxygen content to yield RGO.25 RGO is graphene-like, yet it has an imperfect lattice due to loss of carbon during reduction, residual oxygenated sites, residual sp3-hybridized cycloalkane domains, and the physical grain boundaries between the original GO sheets.21,26 Such defects can reduce conductivity and charge carrier mobility,14 yet RGO has been found useful as a conductor for transistor29 and photovoltaic applications.30,31 Projected advantages of

ABSTRACT Reduced graphene oxide (RGO) is an electrically conductive carbon-based nanomaterial that has recently attracted attention as a potential electrode for organic electronics. Here we evaluate several solution-based methods for fabricating RGO bottom-contact (BC) electrodes for organic thin-film transistors (OTFTs), demonstrate functional p- and n-channel devices with such electrodes, and compare their electrical performance with analogous devices containing gold electrodes. We show that the morphology of organic semiconductor films deposited on RGO electrodes is similar to that observed in the channel region of the devices and that devices fabricated with RGO electrodes have lower contact resistances compared to those fabricated with gold contacts. Although the conductivity of RGO is poor compared to that of gold, RGO is still an enticing electrode material for organic electronic devices possibly owing to the retention of desirable morphological features, lower contact resistance, lower cost, and solution processability.

KEYWORDS: reduced graphene oxide · organic semiconductors · OTFT · compatible interfaces · thin-film morphology · contact resistance
using RGO in these devices compared to traditional materials include high material abundance, high material stability, lower material cost, simpler and less costly processing, and suitability for large area applications.

Previous work in the community has demonstrated the use of graphene-like electrodes for OTFTs. For example, Liu’s group utilized a patterned metal catalyst film to grow few-layer graphene electrodes using a high-temperature (≈ 800 °C) vapor–liquid–solid method and demonstrated good performance in pentacene OTFTs despite of the high roughness of their electrodes. In another example, Müllen’s group reported the patterning of solution-deposited RGO films using oxygen plasma to delineate RGO electrodes and further demonstrated low-contact resistance of these electrodes in pentacene OTFTs. Our work complements these previous reports because we (1) propose several, easily accessible electrode fabrication methods, (2) explore the effects of the fabrication process on the RGO electrode efficiency, (3) demonstrate charge injection into p- and n-channel materials, (4) corroborate the finding of lowered contact resistance compared to gold electrodes, and (5) highlight the need to explore the effect that RGO electrodes have on the growth of organic semiconductor thin-films.

For this study we selected three different organic semiconductors as the active OTFT material: pentacene (p-channel), copper(II) hexadecafluorophthalocyanine (F$_{16}$CuPc) (n-channel), and poly(didodecyldiaryltetrathiophene-alt-didode-cylbithiazole) (PQTBTz-C$_{12}$) (p-channel). The chemical structures of these materials are shown in Figure S1 in the Supporting Information. Thin-films of these materials were deposited onto our RGO electrodes to form BC OTFTs as detailed in the OTFT fabrication and methods sections.

RESULTS AND DISCUSSION

Preparation and Characterization of RGO Films. All water used was 18 MΩ grade. RGO films were spin-coated from aqueous suspensions of GO on cleaned substrates followed by reduction of the GO to obtain RGO. The GO powder was prepared as described previously and in the methods section. Figure 1A is an atomic force microscopy (AFM) image displaying individual GO sheets in a submonolayer film; Figure 1B depicts a typical multilayer film, ~20 nm thick. Several reductive treatments for GO films were investigated as described in Table S1 in the Supporting Information. We selected a reductive treatment consisting of a 3 h thermal annealing at 400 °C in an argon environment because it provided a suitable compromise between process cost, applicability, electrical conductivity, and electrode work function. The resulting RGO material had a typical thickness of ~15 nm, a work function of 5.01 eV, and a four-point probe conductivity of 71 S cm$^{-1}$.

Methodologies for RGO Electrode Patterning. We investigated three different methods of increasing complexity for patterning RGO electrodes in order to determine the best method for patterning RGO for OTFTs. These methods are depicted in Schemes 1–3. Method 1 is the reduce-pattern (R-P) process and it follows the black line in Scheme 1: (1) spin-coat a GO film on a transistor substrate; (2) reduce the film; (3) pattern the RGO film using oxygen plasma and a metal shadow mask. This approach is a simplification of that...
reported by Mullen’s group, and differs from it in two main respects: (i) reusable metal shadow mask replaces the single-use sacrificial Al layer; (ii) the RGO pattern obtained is the negative of the shadow mask, so all RGO features are “shorted” and a method for “disconnecting” them is required. For example, we achieved isolated devices by scoring the RGO film or by cleaving the substrate. This characteristic might restrict the RGO patterns to relatively large and geometrically simple features, but it does not require access to a metal evaporator, so the R-P process may be useful in some settings. OTFT devices fabricated on R-P electrodes showed poor performance, likely due to oxidation of the electrode edges during patterning. Reversing the order of the reduction and patterning (a P-R process that follows the gray line in Scheme 1), greatly improved the electrode performance in OTFT devices because the reduction step reverses the effects of the oxygen plasma on the RGO. We used scanning-electron microscopy (SEM) coupled with Auger electron spectroscopy (AES) to probe the composition of the edges of our R-P and P-R RGO electrodes and found that R-P electrodes indeed show highly oxidized edges compared to P-R electrodes. Figure 2 shows microscopic characterization of these electrodes. To date, we have demonstrated well-resolved electrode gaps as narrow as 2 μm with this fabrication technique.

OTFT Fabrication and Influence of Electrode Material on Organic Semiconductor Morphology. To study the influence of RGO on semiconductor morphology, we prepared large area OTS-modified substrates, unpatterned RGO substrates and substrates bearing 40 nm of evaporated gold. Next we cleaved each large substrate in two pieces and evaporated a 40 nm film of pentacene onto one set of fragments and 40 nm of F16CuPc onto the other. We examined the differences in film morphology using X-ray diffraction (XRD) and AFM, and the results are summarized in Figures 3 and 4. Figure 3A shows XRD spectra from pentacene films deposited on gold, OTS, and RGO substrates. Pentacene deposited on OTS-treated substrates is highly crystalline, and the d(001) spacing found (16.06 Å) corresponds well to that reported in the literature (15.4 Å), indicating that the pentacene molecules deposit edge-on on this surface. Pentacene evaporated onto RGO retains the first two peaks, although with much reduced intensity, indicating that the ordering of the film is less significant, possibly because of surface roughness of the RGO and because of interactions between the electrons of RGO and pentacene that might cause some molecules
to tilt. As expected, pentacene deposited on gold-coated substrates does not contain any of the characteristic peaks of the reported phases, since it is well-known that pentacene deposited on gold grows in a highly disordered three-dimensional phase.\textsuperscript{2,40,41} Figure 3B contains corresponding XRD data for F\textsubscript{16}CuPc films, displaying the same general trend as for pentacene. F\textsubscript{16}CuPc on OTS presents two small peaks, and the film on RGO clearly retains the first peak, but F\textsubscript{16}CuPc on gold does not show any of these peaks likely for similar reasons as discussed for pentacene. These findings suggest that RGO films are more compatible with 2D-growth of semiconductor than gold surfaces and the differences between growth on OTS (contact angle $\approx$ 106\(^\circ\)) and RGO (contact angle $\approx$ 73\(^\circ\)) are likely due to differences in surface roughness, hydrogen content, and surface energy.

Figure 4 summarizes an AFM study of the morphology of pentacene deposited concurrently on OTS, RGO, and gold surfaces to a nominal film thickness of 42 nm. Pentacene on OTS-treated surfaces displayed the expected terraced structure of two-dimensional pentacene plates (Figure 4A). Figure 4B shows the less-ordered, but still two-dimensional (note Z scale) morphology of pentacene deposited on RGO surfaces. In contrast, Figure 4C displays the well-known three-dimensional morphology of pentacene films deposited on gold. These images strongly suggest that films in Figure 4A,B might form better interfaces with contacts than the film in Figure 4C, thus facilitating charge injection into the semiconductor. Figure 4D shows the actual transition region from pentacene deposited on an RGO electrode to pentacene deposited on the OTS-treated active channel. While the morphologies are not identical, pentacene grows two-dimensionally on both surfaces facilitating efficient charge transfer from the semiconductor atop the RGO electrode to the semiconductor deposited on the active channel of the OTFT.\textsuperscript{40,41} Such differences might be relevant when considering the different contact resistances measured in OTFTs bearing RGO and gold electrodes since the morphological changes of the pentacene film from electrode to channel are much more drastic in the latter case.

Comparison of Transistor Performance of OTFTs with RGO or Gold Electrodes. We fabricated OTFTs bearing RGO electrodes from each of the three methods discussed above. Devices with R-P electrodes performed poorly, but all other devices showed comparable performance.
because patterned RGO is identical after the reduction step. The analysis below focuses on OTFTs fabricated using photolithographically patterned RGO because the length and width of the active channel can be precisely controlled with this fabrication method.

Figure 5 shows a transfer-line method (TLM)\textsuperscript{42–44} plot that was used to estimate the contact resistances of pentacene/RGO and F\textsubscript{16}CuPc/RGO, pentacene/gold, and F\textsubscript{16}CuPc/gold devices. The aspect ratio of the active OTFT channel (width of the channel divided by its length, \( W/L \)), was kept constant at a value of 20 for all devices. We found that our estimated contact resistance for BC pentacene/gold OTFTs (\( \sim 1 \times 10^6 \) \( \Omega \) cm) correlates well with literature values, which vary in the range \( 4 \times 10^4 \) to \( 7 \times 10^6 \) \( \Omega \) cm depending on the semiconductor film thickness and deposition conditions.\textsuperscript{42,45} RGO electrodes show \( \sim 100 \times \) lower contact resistance for charge injection into the selected organic semiconductors than gold electrodes (SAM-modified gold electrodes have lower contact resistances because of their different surface dipoles and energies).\textsuperscript{10,46} This finding may, at first, seem counterintuitive since the resistance of the RGO electrode itself is \( \sim 6 \times 10^3 \) times higher than that of gold (Table S1 in Supporting Information). However, the parameter being evaluated is not the transfer of charge carriers through the electrode, but the transfer of charge carriers across the electrode/semiconductor interface and across the organic semiconductor transitioning from the electrode into the channel region of the OTFT. Higher contact resistances can be expected between organic semiconductors and metals due to the interface dipole barrier that forms when \( \pi \)-electrons from conjugated molecules adsorb on metal surfaces. These electrons push back electron density from the metal surface and can effectively lower the surface-dipole contribution to the metal work function by as much as 0.5–1.0 eV. Interorganic systems, such as our RGO/organic semiconductor, are not as susceptible to these effects since RGO has significantly lower surface electron density compared to a metal, resulting in RGO’s workfunction having only a small surface dipole contribution to it.\textsuperscript{47} Other carbon-containing materials have also been shown to have lower contact resistance than gold for charge injection into organic semiconductor materials.\textsuperscript{29,48} A common feature in all these observations is that the carbon-based electrode is electron donating and the organic semiconductor is electron-accepting relative to the elec-
trode. Such interorganic interfaces have been shown to have enhanced charge transport.49 Beyond electronic effects, our film morphology studies suggest that unlike gold, RGO allows the formation of smooth 2D-grains at the electrode/semiconductor interface, likely yielding improved connectivity with grains growing at the OTS-treated active channel and facilitating better charge transfer into the channel. Thus the lowered contact resistance we observe might have various contributing factors that will need to be elucidated and optimized elsewhere. In the future, other factors that could lead to further reductions in contact resistance include controlling the crystallinity and morphology of the semiconductor film,10,46 performing postreductive treatment of the RGO surface with appropriate SAMS,46,47 and doping the RGO material.

Next we characterized the electronic performance of OTFTs bearing photolithographically patterned RGO electrodes. Figure 6 panels A, C, and E display the transfer curve characteristic, or the plot of drain-source current ($I_{DS}$) vs gate voltage ($V_G$), for OTFTs where the active layer is a film of (A) pentacene, (C) F16CuPc, and (E) PQTBz-C12, respectively. In each case the curve is well behaved, has a clear on–off transition, an $I_{ON}/I_{OFF}$ ratio $> 10^6$, and a reasonably low threshold voltage ($V_{th}$) for BC devices on 300 nm silicon dioxide dielectrics. The field-effect mobilities (FET-$\mu$) extracted from the $I$–$V$ curves of our nonoptimized devices are $2.26 \times 10^{-3}$ for pentacene, $3.06 \times 10^{-2}$ for F16CuPc, and $1.43 \times 10^{-2}$ cm$^2$ V$^{-1}$ s$^{-1}$ for PQTBz-C12. The mobilities for pentacene and F16CuPc OTFTs are of the same order of magnitude as those reported in the literature (ca. $5 \times 10^{-1}$ and ca. $3 \times 10^{-2}$ cm$^2$ V$^{-1}$ s$^{-1}$ for BC pentacene$^{49}$ and F16CuPc$^{33}$ OTFTs, respectively). Our BC PQTBz-C12/RGO devices showed significantly lower FET-$\mu$ than the recently reported top-contact PQTBz-C12/gold ($3.3 \times 10^{-1}$ cm$^2$ V$^{-1}$ s$^{-1}$),24 yet, top-contact OTFTs typically show improved performance over BC devices due in
part to film-morphology considerations. As will be shown below, our BC PQTBTz-C12/RGO devices did achieve higher FET-μ than corresponding BC PQTBTz-C12/gold controls. These observed improvements in OTFT performance are likely due at least in part to the influence of RGO electrodes on the morphology of the semiconductor thin-film, which might facilitate charge injection. A recent report describing the use of RGO as a gold-modification layer in BC pentacene OTFTs also sees the pentacene curves (Figure 6B) have a sublinear than the corresponding transfer curves. As such we can more information regarding the physics of the devices.

Table 1: Comparative Transistor Performance of RGO and Gold-Based OTFT Devices

<table>
<thead>
<tr>
<th>Material</th>
<th>Contact</th>
<th>I_DON</th>
<th>av FET-μ</th>
<th>max FET-μ</th>
<th>V_TH</th>
<th>I_ON/I_OFF</th>
</tr>
</thead>
<tbody>
<tr>
<td>pentacene</td>
<td>RGO</td>
<td>1.19 × 10^-4 ± 9%</td>
<td>1.80 × 10^-1 ± 14%</td>
<td>2.11 × 10^-1</td>
<td>-7.0 ± 0.6</td>
<td>5.23 × 10^6</td>
</tr>
<tr>
<td></td>
<td>gold</td>
<td>9.95 × 10^-4 ± 9%</td>
<td>1.05 × 10^-2 ± 0.2%</td>
<td>1.05 × 10^-2</td>
<td>-1.9 ± 3.8</td>
<td>5.75 × 10^5</td>
</tr>
<tr>
<td>F16CuPc</td>
<td>RGO</td>
<td>1.60 × 10^-1 ± 26%</td>
<td>2.76 × 10^-2 ± 23%</td>
<td>3.30 × 10^-2</td>
<td>26.1 ± 3.4</td>
<td>1.00 × 10^7</td>
</tr>
<tr>
<td></td>
<td>gold</td>
<td>4.41 × 10^-2 ± 17%</td>
<td>1.10 × 10^-1 ± 25%</td>
<td>1.38 × 10^-3</td>
<td>38.7 ± 1.0</td>
<td>6.23 × 10^5</td>
</tr>
<tr>
<td>PQTBTz-C12</td>
<td>RGO</td>
<td>6.34 × 10^-3 ± 75%</td>
<td>8.96 × 10^-3 ± 77%</td>
<td>1.47 × 10^-2</td>
<td>-11.1 ± 9.9</td>
<td>1.04 × 10^8</td>
</tr>
<tr>
<td></td>
<td>gold</td>
<td>4.65 × 10^-3 ± 13%</td>
<td>1.07 × 10^-2 ± 15%</td>
<td>1.20 × 10^-3</td>
<td>-24.7 ± 8.4</td>
<td>3.54 × 10^9</td>
</tr>
</tbody>
</table>

1. Average drain-source current at the end maximum of the transfer curve, given in amps, dispersion indicated as a relative standard deviation (RSD).
2. Average field-effect mobility given in cm^2 V^-1 s^-1.
3. Maximum field-effect mobility measured on that material, given in cm^2 V^-1 s^-1.
4. Average threshold voltage of OTFT operation, given in volts.
5. Average ratio of the I_DON currents in the ON and in the OFF state.
ecules of the conjugated polymer which tend to form amorphous films and can be less sensitive to the electrode surface.

CONCLUSIONS

We demonstrated a versatile approach for the fabrication of RGO electrodes including solution processing of unreduced GO and patterning of the same using oxygen plasma or photolithography. We evaluated several reductive methods to form RGO from GO and studied their effect on the properties of RGO as an electrode material. We also characterized the effect of the RGO surface on the morphology of overlaying organic thin-films. Functional p- and n-channel OTFT with RGO electrodes were fabricated using small-molecule and polymer semiconductors. Bottom contact devices with RGO electrodes displayed lower contact resistance and higher mobilities than similar OTFTs with gold electrodes. Future research directions may include the detailed study of molecular orientation at the RGO interface, determination of the magnitude and effect of surface RGO dipoles, functionalization and doping of RGO electrodes to increase their conductivity and to further improve charge injection, and comparison of the performance of RGO electrodes with Al or Mo electrodes for n-channel materials. Importantly, our current findings suggest that notwithstanding their high electrical resistance compared to gold, RGO electrodes may be suitable for the fabrication of large area organic electronic devices owing to the abundance and relatively low cost of the starting material, their facile and relatively low-cost processing, and the possibility for nanometer-scale functionalization and control of individual GO sheets.

METHODS

Preparation of Water-Soluble Graphene Oxide Powder. Graphene oxide was prepared using modified Hummers method from flake graphite (average particle diameter of 4 μm, 99.95% purity, Qingdao Tianhe Graphite Co. Ltd., Qingdao, China). Briefly, 5 g of graphite and 3.75 g of NaNO₃ as received (A.R.) were placed in a flask. Then, 375 mL of H₂SO₄ (A.R.) was added with stirring in an ice-water bath, and 22.5 g of KMnO₄ (A.R.) were slowly added over about 1 h. Stirring was continued for 2 h in the ice-water bath. After the mixture was stirred vigorously for 5 days at room temperature, 700 mL of 5 wt % H₂SO₄ aqueous solution was added over about 1 h with stirring, and the temperature was kept at 98 °C. The resultant mixture was further stirred for 2 h at 98 °C. The temperature was reduced to 60 °C, 15 mL of H₂O₂ (30 wt % aqueous solution) was added, and the mixture was stirred for 2 h at room temperature. Next, ions of oxidant and other inorganic impurity were removed repeating the following procedure: centrifugation, removal of the supernatant liquid, addition of 2 L of a mixed aqueous solution of 3 wt % H₂SO₄/0.5 wt % H₂O₂ to the bottom solid, and dispersion of the solid using vigorous stirring and bath ultrasonication for 30 min at a power of 140 W. Then a similar procedure was repeated three times using 3 wt % HCl aqueous solution (2 L) and one time using H₂O (2 L). The resultant water solution was passed through a weak basic ion-exchange resin (D301T, Nankai University Chemical Plant) with water as mobile phase to remove the remaining HCl. Then water was removed through a drying process for the collected solution to yield 3.5 g of product.

Substrate Preparation and Deposition of GO Films. For basic transistor substrates we used highly doped n-type (100) Si wafers (<0.004 Ω cm) with a 300 nm dural thermal oxide gate dielectric (capacitance Cₓ = 10 nF cm⁻²) and cleaned them in piranha solution (7:3 H₂SO₄:H₂O₂ mixture, CAUTION: extremely corrosive and highly exothermic) for 40 min followed by extensive rinsing with deionized water and storage under water until the moment of RGO deposition. For OTS-SAM sacrificial layer substrates, a 0.1% solution of octadecyl-trime-thoxysilane (Gelest Inc., Morrisville, PA) in trichloroethylene (EMD Chemical Inc., Darmstadt, Germany) was spin-coated on the cleaned wafers and allowed to react overnight at room temperature in the presence of ammonia vapor. Excess silane was removed by ultrasonication in toluene, followed by rinsing with toluene, acetone and isopropanol alcohol, and drying under a stream of nitrogen. OTS-treated wafers typically showed a contact angle of approximately 105°. Patterned photoresist substrates were prepared in a cleanroom using standard photolithography techniques. The patterned and developed photoresist-coated transistor substrates were then kept in sealed containers and subjected to a brief, 20 s oxygen plasma treatment (200 W, 150 mTorr O₂) to activate the exposed silicon dioxide surfaces. Etching of RGO for fabrication of P-R and R-P electrodes was performed by exposure to oxygen plasma with slightly harsher conditions: 200 W, 200 mTorr O₂, and 120 s.

GO was deposited on freshly cleaned basic transistor substrates or on freshly patterned OTS-SAM substrates by spin-coating. First, these substrates were dried using high spin rates. Then a volume of aqueous GO dispersion (~3 mg/mL) sufficient to cover the whole substrate was allowed to rest on the substrate for 15 s, after which the spin-rate was increased from 0 to 1200 rpm in a linear fashion over 60 s. Films were dried by placing them on a hot plate at 110 °C for 30 min before any reducing treatments. Deposition of GO films on photoresist-coated differed in that the films were dried for 1 min at 110 °C before a lift-off step in warm acetone, after which the films were dried again on a hot plate at 110 °C for 30 min.

GO Reduction Treatments. Hydrazine Vapor Reduction. GO films on substrates were placed in a clean glass Petri dish nested in a larger glass Petri dish which also contained 1 mL of hydrazine monohydrate 98% (Alfa Aesar, Ward Hill, MA). The larger dish was covered with a glass lid, sealed with Parafilm tape, and placed over a hot plate at 40 °C for 18 h, after which the dish was opened and the films were rinsed with purified water and dried both under a nitrogen stream and by heating to 80 °C in vacuum. GO films changed color after the hydrazine vapor treatment, from matte brown to metallic gray, indicating reduction of the material.

Thermal Annealing at 400 °C under Argon Flow. Dry GO films on substrates were loaded inside a 2 cm internal diameter cylindrical quartz boat with open ends. The boat was introduced in a 1 in. internal diameter glass tube oven fitted with controlled vacuum and gas flow. Films were heated under a continuous flow of 70 standard cubic centimeters of ultrapure argon, at a rate of 20 °C/min, held at 400 °C for 3 h, and allowed to cool to room temperature over 1 h.

Graphitization in Vacuum at 1100 °C. Dry GO films on substrates were placed in quartz boats inside a 3 ft long 1 in. diameter quartz tube with one end closed. The tube was introduced into a Lindberg/BlueM split hinge oven (Lindberg/Blue M 3-zone tube oven, Blue-M, White Deer, PA) and the open end was fitted to a turbopump vacuum line (Turbo-V 250 MacroTorr, Varian Inc., Palo Alto, CA). Films were heated to 100 °C at ambient pressure, then the turbo pump was switched on and a vacuum of 10⁻⁸ Torr was established before heating to 1100 °C. Heating rates as high as 20 °C/min could be achieved without loss of films. The temperature was held constant at 1100 °C for 3 h after which the system was allowed to cool down (3 h).

Deposition of Organic Semiconductor Materials. Small molecule organic semiconductors were simultaneously deposited onto RGO, OTS-SAM and gold surfaces using an Angstrom thermal evapo-
and were subsequently annealed by heating to 180 °C for 1 h
in hydrous chlorobenzene (Sigma-Aldrich). These polymer films
were deposited onto a room temperature substrate by spin-coating from a 3 mg/mL solution in anhydrous chlorobenzene (Sigma-Aldrich). These polymer films were dried by heating them for 3 h inside a vacuum oven at 80 °C and were subsequently annealed by heating to 180 °C for 1 h in a dry N2 environment followed by slow cooling to room temperature.

OUTF Measurements. The OUTF transfer and output characteris-
tics were recorded in air using a Keithley 4200 semiconductor
parametric analyzer (Keithley Instruments, Cleveland, OH).

Characterization of Film Topography and Composition. Tapping-mode
AFM investigation of the films was accomplished using a Multi-
mode NanoScope III with Extender electronics (Digital Instru-
mements/Veeco Metrology Group, Santa Barbara, CA). Film thick-
ness measurements were performed with a Dektak 150 profiometry (Veeco Metrology Group). Auger electron spectra (AES) were collected with a PHI 700 Scanning Auger Nanoprobe (Physical Electronics, Inc.) equipped with secondary electron imaging
and 10 nm Auger resolution with high elemental sensitiv-
ity. XRD analysis was completed as follows: We deposited 40 nm pentacene and 50 nm F16CuPc films on sets of freshly prepared
ROG, OTS-SAM, and gold-coated substrates. These films were
analyzed using a Philips PANalytical X’Pert diffractometer using the Cu Kα line. Work function measurements were performed on
large area thin-films of the material of interest supported on sili-
con dioxide substrates using a Riken Keiki PES system model
AC-2.

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Supporting Information Available: Materials used in this study, characterization of GO reduction methods and electrode edges. This material is available free of charge via the Internet at http://pubs.acs.org.

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Fabrication and Evaluation of Solution-Processed Reduced Graphene Oxide Electrodes for p- and n-Channel Bottom-Contact Organic Thin-Film Transistors

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Supporting Information

Materials used in this study

To evaluate the applicability of our RGO electrodes to organic electronics we chose to work with three different organic semiconductor systems: thermally evaporated pentacene, a p-channel small-molecule semiconductor, thermally evaporated semiconductor copper (II) hexadecafluorophthalocyanine (F_{16}CuPc),35 an n-channel semiconductor, and solution-processed
poly(didodecylquaterthiophene-alt-didodecylbithiazole) (PQTBTz-C_{12}), a p-channel conjugated polymer. The chemical structures of these materials are shown in Figure S1. Thin-films of these materials were deposited onto our RGO electrodes to form BC OTFTs as detailed in the OTFT fabrication and methods sections.

Figure S1. Chemical structures of the organic semiconductors used to explore the material compatibility with RGO electrodes.

**Characterization of GO reduction methods**

The selection of the reduction method came as a compromise between process cost, process applicability, electrode conductivity and electrode work function. We prepared a large area 21 nm GO film on a SiO$_2$/Si substrate and cleaved the substrate into four pieces, which were reduced and characterized as indicated in Table S1.

Each fragment was subsequently divided in 2 pieces, and the work function of the material was measured from the first piece. Gold electrodes were deposited on the second piece to perform four-point probe measurements, from which the conductivity of the film was calculated. The results of these measurements, and the comparison to a 40 nm evaporated gold control film are also listed in Table 1. The variation in film conductivity is tremendous, spanning nearly nine orders of magnitude for the graphene-based materials and is highly dependent upon the GO reduction process conditions. The non-
reduced film is an extremely poor conductor. The hydrazine-treated film, which requires a minimum energy investment during the reduction, offers a significantly enhanced conductivity, and the method is compatible with a wide variety of substrate materials since the reduction occurs below 100°C. Unfortunately, the conductivity of this RGO material is still too low for an electrode application. The sample annealed to 400°C is at least seven orders or magnitude more conductive than the non-reduced film, and 10,000 times more conductive than the hydrazine-RGO sample. While the energy required for the reduction is substantial, it is much less than that required for graphitization, and the temperature is still compatible with a number of substrates including glass. The conductivity of the graphitized film is closest to that of the gold control among all the RGO films; however, this value with is still two to three orders of magnitude inferior to gold.

Table 1. Summary of GO Reduction Methods.

<table>
<thead>
<tr>
<th>Fragment</th>
<th>GO Reduction process</th>
<th>Work Function /eV</th>
<th>Conductivity /Scm⁻¹</th>
<th>Thickness loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>None</td>
<td>5.30</td>
<td>7.30 x10⁻⁶</td>
<td>0%</td>
</tr>
<tr>
<td>2</td>
<td>Hydrazine vapor, 18 hr 40 °C</td>
<td>4.83</td>
<td>1.00 x10⁻²</td>
<td>14%</td>
</tr>
<tr>
<td>3</td>
<td>Thermal anneal: 3hr, 400 °C, Ar flow.</td>
<td>5.01</td>
<td>7.07 x10¹</td>
<td>19%</td>
</tr>
<tr>
<td>4</td>
<td>Graphitization, 3hr, 1100 °C, 10⁻⁵ Torr</td>
<td>4.82</td>
<td>2.53 x10³</td>
<td>27%</td>
</tr>
<tr>
<td>Gold reference</td>
<td>None</td>
<td>4.77</td>
<td>4.52x10⁵</td>
<td>N/A</td>
</tr>
</tbody>
</table>

The work function of the RGO materials, measured using ultraviolet-photoelectron emission spectroscopy (UPS), appears to be inversely correlated with the conductivity of the film, decreasing significantly from 5.30 eV for the GO film, to 4.82 eV for the graphitized sample. The decrease of the work function is likely due to the gradual disappearance of strongly electronegative oxygenated groups throughout the thickness of the film and to the increasing availability of π-electrons within the film as
the graphene lattice is regenerated. Interestingly, the work function of hydrazine-RGO is rather low, possibly due to the presence of lone-pair electrons from nitrogen atoms incorporated into the RGO film as hydrazones. After this analysis we decided to reduce all our GO films using the 400°C thermal annealing method (conductivity $\approx 71 \ \text{Scm}^{-1}$, work function $\approx 5.01 \ \text{eV}$) since it provided a balance of electrode conductivity, work function, energy cost and process applicability. The resistivity of the materials shown in the table is calculated as the inverse of the conductivity and thus, our thermally reduced RGO electrodes (line 3) are about $6.4 \times 10^3$ times more resistive than gold.

**Chemical Characterization of the Edges of R-P and P-R RGO Electrodes:**

Scanning-electron microscopy (SEM) coupled with Auger electron spectroscopy (AES) was used to probe the composition of the edges of our R-P and P-R RGO electrodes and the results are summarized in Figure S2. We found significant re-oxidation of the RGO electrode sidewalls in the R-P process, with a relatively wide transition region between the gap and the unaffected RGO as determined by AES. This wide transition can be attributed to underetching of the RGO during the plasma treatment, and the result is exacerbated by any physical separation between the etch mask and the RGO film. Deposition of a masking layer directly on the RGO as in the case of Müllen’s report, 1 can significantly reduce the lateral extent of the undercut but may degrade the surface of the RGO. We therefore avoided the R-P method for device fabrication.
Figure S2. Film composition at the electrode edges for R-P and P-R RGO electrodes. (A) SEM micrograph of typical electrodes studied. The RGO and SiO$_2$ regions are indicated and the gap between electrodes is $\approx 50 \, \mu$m. The dashed red line indicates the analysis path for collection of AES data shown in (B-C) with the position of the edge roughly corresponding to the 50 $\mu$m mark. (B) Normalized AES carbon (top panel) and oxygen (bottom panel) signals as a function of position for an R-P and a P-R electrode. For carbon the R-P shows a wide transition region between the gap (left) and the electrode (right), while in the P-R the change occurs over about half the distance. Oxygen should only be detectable in the gap (left), but the R-P trace shows a gradual decrease of O$_2$ signal at the gap/electrode edge with significant oxygen content well into the electrode region (right). The P-R electrodes display a
sharp decrease in O₂ signal narrowly centered about the expected position of the edge.

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