High Mobility, Printable, and Solution-Processed Graphene Electronics

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ABSTRACT The ability to print graphene sheets onto large scale, flexible substrates holds promise for large scale, transparent electronics on flexible substrates. Solution processable graphene sheets derived from graphite can form stable dispersions in solutions and are amenable to bulk scale processing and ink jet printing. However, the electrical conductivity and carrier mobilities of this material are usually reported to be orders of magnitude poorer than that of the mechanically cleaved counterpart due to its higher density of defects, which restricts its use in electronics. Here, we show that by optimizing several key factors in processing, we are able to fabricate high mobility graphene films derived from large sized graphene oxide sheets, which paves the way for all-carbon post-CMOS electronics. All-carbon source–drain channel electronics fabricated from such films exhibit significantly improved transport characteristics, with carrier mobilities of 365 cm²/(V·s) for hole and 281 cm²/(V·s) for electron, measured in air at room temperature. In particular, intrinsic mobility as high as 5000 cm²/(V·s) can be obtained from such solution-processed graphene films when ionic screening is applied to nullify the Coulombic scattering by charged impurities.

KEYWORDS Graphene, high mobility transistor, solution-processed, printable electronics, ionic screening, doping, impurity scattering

The discovery of graphene has revolutionized the field of electronics owing to its excellent electronic properties and chemical and mechanical stability, which paves the way for ultrafast electronic devices and bio- and chemical sensors.1,2 The mechanical exfoliation, or “Scotch tape” method, has been used to produce the first high-quality graphene sheets which set the performance standard for graphene produced by other methods. However, the “Scotch tape” method is not compatible with large-scale industrial processing and precludes the widespread implementation of graphene electronics; thus there are intense efforts worldwide to discover upwardly scalable production methods for high-quality graphene. Recent breakthroughs include the large-area deposition of few-layer graphene (FLG) using chemical vapor deposition on catalyst-coated substrates.3 Another research thrust involves the solution processing of graphene derivatives. Chemical exfoliation methods which produce graphene oxide from graphite result in high-yield production of single sheet dispersions.4,5 The solution-processability of GO offers unique advantages since it is readily amenable to spin-coating, spray-casting, drop-casting, or inkjet printing onto substrates for large-scale production of graphene electronic circuits. The deoxidation of graphene oxide (GO) by chemical reduction and thermal annealing has been shown to produce zero-band-gap semi-metal graphene nanosheets which can exhibit trap-free band transport despite defects and disorder.6 However, the transistor carrier mobility in such a GO-derived graphene thin film is usually between 0.1 and 1 cm²/(V·s) as reported in literature,4,6,7 which is several orders lower than that of the mechanically cleaved graphene. There are several possibilities for the poor performance in these chemically processed graphene (CPG). The charge percolation is limited by disconnected network of π-delocalized tracks in these CPG. Defects created after the removal of C–O functional groups hinder the full recovery of the charge transport properties of pristine graphene8 and further processing is needed to recover the extended aromatic framework. Therefore, there are still significant challenges ahead before CPG can be used in high mobility electronic devices.

In this work, we discovered that by optimizing several key factors in film processing and device fabrication, unprecedented performance in the electrical transport properties of CPG can be obtained. Our results reaffirm that CPG retains the intrinsic structural coherence for high mobility transport. Building upon this, we have also explored the premise of using CPG for inkjet printable all-carbon electronics.

For electronic applications, the mobility and conductivity of graphene sheets are critical.8 However it is widely known that the electrical characteristics of CPG are generally very poor. A survey of most reports found that a large percentage of CPG consists of GO flakes with sizes 1 µm or less due to prolonged ultrasonication and harsh oxidation treatment of the colloidal GO suspension.4–11 We have a simple hypoth-
esis. We propose that the poor electrical characteristics can be circumvented by using big sized GO (BSGOS) with lateral size above 25 µm. Submicrometer sized GOs synthesized by harsh oxidation conditions have a higher density of defects relative to BSGOs, due to the fact that the generation of smaller sized sheets from larger sized ones involves chemical destruction of aromatic bonds. The density of these defects may scale in a nonlinear way with the area of GOs; smaller GOs have a significantly larger density of disorder on the basal planes due to a higher composition of nonstoichiometric oxygen. Another important implication in transport measurement is that for an edge-to-edge continuous film constructed from networks of graphene flakes, the larger flakes should give a lower number of sheet-to-sheet junctions compared to the smaller flakes within a fixed channel length.

Here we report a reproducible and simple method to obtain high-quality BSGO (Figure 1a) where more than 20% of the flakes have lateral dimension larger than 25 µm, according to size-counting using optical micrograph and scanning electron microscopy (SEM) images. Our method is based on the modified Hummer’s method. We applied careful gradient separation and minimized the number of sonication steps to avoid breaking up the larger sized GO sheets. Such BSGO sheets possess a significantly reduced number of C–O groups compared to small-sized GO, as evident from the relative proportion of the C–C bond versus C–O bonds in the deconvoluted X-ray photoelectron spectroscopy (XPS) spectra. The deconvoluted area assignable to the C–C bonds of graphene is higher than that of small-sized GO by 10%. Despite a lower proportion of C–O groups, the aqueous solution of BSGO remains stable and opaque over several months in concentrations as high as 50 mg mL\(^{-1}\). (Figure 1b). In addition, spin-coating of the BSGO solution onto a SiO\(_2\)/Si substrate allows the formation of a uniform, continuous graphene thin film as shown in Figure 1c where the film morphology probed by atomic force microscopy (AFM) shows incommensurately stacked BSGO sheets with the edges of individual GO sheets clearly visible. By varying the concentration of BSGO solution, we are able to tune the thickness of the graphene film selectively from one to three layers. Upon thermal annealing of BSGO-coated SiO\(_2\)/Si substrate at 1000 °C, the C 1s peak signal assignable to the C–C bonds of graphene increases from 53% to 89%. AFM measurement also indicates a reduction of sheet thickness from ∼1 nm, due to protruding oxygen groups on either side of GO sheets, to 0.53 nm, a characteristic thickness of graphene sheet (see Figure S3 in Supporting Information). Significant structural changes reflective of the restoration of delocalized \(\pi\)-conjugation in GO-derived graphene sheets are also evident from their Raman spectra (Figure 1d). The G band for reduced BSGO is sharper and shifts to lower frequency (1586 cm\(^{-1}\)) as compared to BSGO (1594 cm\(^{-1}\)). The ratio of Raman D to G band intensity (\(I_D/I_G\)) decreases from 0.81 to 0.78, thus indicating an increase in the average size of sp\(^2\) domains on reduced BSGO. The restoration of the \(\pi\)-conjugated structure in the BSGO sheets translates to a high conductivity of 760 S/cm, which is close to that of polycrystalline graphite (1250 S/cm) (see Figures S4 and S5 in Supporting Information). This makes these graphene sheets an attractive candidate for making continuous, highly conducting graphene thin films by spin-coating or printing technologies amenable to large scale processing.

To investigate the transport characteristics of these graphene films, we fabricated graphene thin film field-effect
transistors (FET) with BSGO of varying thickness ranging from one to three layers (Figure 2). The thickness and uniformity of the graphene film were verified statistically by optical contrast spectroscopy and AFM. Clear contrast difference for single-layer, bilayer, and trilayer graphene films deposited on a SiO$_2$/Si surface with SiO$_2$ thickness of 285 nm can be observed from the contrast spectra generated by measuring the reflection spectra of white source light. In addition, tapping mode AFM topographical section analysis was done randomly on 10 different areas of the SiO$_2$/Si substrates (1 cm by 1 cm) which are coated with single-layer, bilayer, and trilayer graphene film to evaluate the thickness and surface area coverage of graphene film. Graphene film thickness ($x$) for single-layer graphene device is $0.5 < x \leq 0.8$ nm with a surface area coverage of $78 \pm 8\%$, bilayer graphene device is $0.8 < x \leq 1.6$ nm with surface area coverage of $80 \pm 7\%$, and trilayer graphene device is $1.6 < x \leq 2.4$ nm with surface area coverage of $60 \pm 5\%$ (see Figure S8 in Supporting Information). Oxygen plasma was used to etch the graphene layers outside the active channel to reduce leakage current, which did not exceed 100 pA. The charge transport behavior of all graphene thin film FETs is representative of the typical transport characteristic of individual mechanically cleaved graphene sheet as evi-

FIGURE 2. Single sheet graphene and thin graphene-based film field-effect transistor (FET). (a) Optical image of about single-layer reduced BSGO thin film with overlapping edges. (b) The transfer characteristics of single-layer reduced BSGO thin film FET with channel width $W \sim 31.8$ µm, channel length $L \sim 26.92$ µm, and hole and electron mobility of 5.4 and 1.1 cm$^2$/V·s, respectively, at constant $V_{ds}$ of 1 V. Inset shows the two-point probe measurement of the single-layer reduced BSGO thin film FET. Scale bar corresponds to 20 µm. (c) Optical image of bilayer reduced BSGO thin film. (d) The transfer characteristics of bilayer reduced BSGO thin film FET with channel width $W \sim 32.55$ µm, channel length $L \sim 30.00$ µm, and hole and electron mobility of 50 and 10 cm$^2$/V·s, respectively, at constant $V_{ds}$ of 10 mV. Inset shows the schematic representation of the reduced BSGO thin film FET. (e) Optical image of about trilayer reduced BSGO thin film. (f) The transfer characteristics of trilayer reduced BSGO thin film FET with channel width $W \sim 29.87$ µm, channel length $L \sim 32.11$ µm FET, and hole and electron mobility of 92 and 51 cm$^2$/V·s, respectively at constant $V_{ds}$ of 10 mV. Inset shows the schematic representation of the reduced GO thin film FET. The thickness of gate dielectric SiO$_2$ for all FETs is 285 nm.
denced from the ambipolar behavior (panels b, d, and f of Figure 2). The conductivity obtained for single-layer, bilayer, and trilayer graphene film is 58, 124, and 150 S/cm, respectively. Electron and hole mobility can be extracted from the linear regime of the transfer characteristics, using 

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\mu = \frac{[(\Delta I_{ds}/\Delta V_{ds})(L/W)]/C_{ox} \Delta V_g}{I_{ds}, V_{ds}, and V_g are drain-source current, drain-source voltage and gate voltage, respectively. From the \( I-V_g \) curves, we derive a maximum hole and electron mobility of 5.4 and 1.1 cm²/(V·s) for the single-layer graphene film device, 50 and 10 cm²/(V·s) for the bilayer graphene film device, and 92 and 51 cm²/(V·s) for the trilayer graphene film device, respectively. These values are significantly larger than the reported field effect transistor mobilities of thin films derived from CPGs, thus substantiating that the high temperature annealing and large-sized GOs in our case allow 2D charge percolation of the extended \( \pi \)-electron network. The \( \pi \)-electron systems in the CMGs are disconnected due to regioselectivity in the deoxidation process, and a high temperature thermal annealing at 1000 °C is needed to allow the coalescence of the initially isolated \( \pi \)-electron network. However, although these values are significantly larger than those reported for CPG thin films, they are still at least 3 orders of magnitude lower than those derived from mechanically cleaved graphene. Hence, the limiting factors affecting charge carrier mobility were investigated in the following sections.

The advantage of the solution-processable GOs is that they can be used to create large-scale all-carbon electrodes via inkjet printing. This offers unique advantages over chemical vapor deposition method since no pre-patterning of catalysts is needed. Such graphene electrodes allow all-carbon contacts to be fabricated on graphene. Figure 3 illustrates a schematic representation of two types of fabrication processes for printable graphene electrodes. In Figure 3a–d, thick graphene electrodes are first drop-cast (or printed) onto SiO₂/Si substrate followed by spin-coating, drop-casting, or printing a thin layer of graphene over these electrodes to form all-carbon junctions. Figure 3e–h illustrates the combination of photolithography and conventional processes typically employed in the semiconductor industry. First, narrow channels with width of 2 \( \mu \)m are defined by photolithography. Next, graphene solution is drop-cast (or printed) onto SiO₂/Si substrates followed by spin-coating, drop-casting, or printing a thin layer of graphene over these electrodes to form all-carbon junctions. Figure 3i–k illustrates the combination of photolithography and conventional processes typically employed in the semiconductor industry. First, narrow channels with width of 2 \( \mu \)m are defined by photolithography. Next, graphene solution is drop-cast (or printed) onto these channels which are subsequently annealed at 150 °C for 20 min to improve adhesion of GO electrodes onto the SiO₂/Si substrate. This device is then immersed in acetone to remove the photoresist by short time sonication. These remaining delineated GO ele-
trodes after lift-off were vacuum annealed at 1000 °C. Highly conducting graphene electrodes derived from BSGO are about 50-100 nm thick with conductivity in the order of 650 S/cm. We observed an enhancement in both hole and electron mobility (365 and 281 cm²/(V·s), respectively) by over an order of magnitude for these all-carbon FET devices compared to hole and electron mobility (92 and 51 cm²/(V·s), respectively) obtained from thin graphene film devices made with gold electrodes.

This provides a crucial clue that the reduction in contact resistance offered by graphene electrodes can be a key factor for mobility enhancement. It is also interesting to note that the asymmetric factor, which is the ratio of hole to electron mobility, is significantly reduced when gold electrodes on graphene are replaced by printed graphene electrodes. Such asymmetric mobility is speculated to be due to two main factors. One, impurity doping by the underlying silicon dioxide substrate results in different scattering cross sections for graphene carriers by charged impurities. Negatively charged impurities and siloxyl groups on silicon oxide have been found to p-dope single-layer graphene and organic thin-film transistors. This effect is especially deleterious at the Dirac point (which defines the threshold voltage) since the screening of charged impurities is weak due to lower carrier concentration. Two, charge transfer at the graphene/metal interface could result in a p-no rp heterojunction depending on the polarity of carriers in bulk graphene sheet. Therefore, we believe that interfacial π−π interactions allow better adhesion of graphene electrodes onto graphene active channels which significantly reduces contact resistance and improves carrier mobilities and the decrease in the asymmetric factor also stems from the removal of p−n or p−p heterojunction created by the graphene/metal interface. Another interesting observation is the replacement of gold electrodes with graphene electrodes results in a pronounced effect of short-range scattering which is characterized by the transition from linear conductivity dependence at low gate voltage to a constant conductivity at high gate voltage (Figure 4a). The overall conductivity of the device is contributed by (i) long-range conductivity (σ_L) which is influenced by long-range scatterers such as charged impurities on substrates and (ii) short-range conductivity (σ_S) attributed to the metal/graphene interface or atomic and edge defects on graphene. Therefore, the overall conductivity is expressed as

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\sigma^{-1} = \sigma_L^{-1} + \sigma_S^{-1} = (\mu C_g |V_g - V_{g,min}|^{-1}) + \sigma_S^{-1}
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in which \(\mu\) is the carrier mobility, \(C_g\) is gate capacitance, \(V_g\) is gate voltage applied, and \(V_{g,min}\) is threshold voltage at the Dirac point. Since both electrodes and active channels are made up of large amount of incommensurately stacked graphene sheets, we attribute the short-range conductivity, which results in sublinear behavior at smaller \(|V_g - V_{g,min}|\) range, to edge defects of multiple overlapping graphene sheets. This results in the short-range conductivity dominating the transport property of our device at a much lower gate voltage range than devices made from gold electrodes.

![Graphene FET Device](image_url)
Several possibilities for the types of scatterers as well as scattering mechanisms, which could potentially limit charge carrier transport, have been discussed in terms of electron–phonon scattering, thermal activation barrier of carriers, electrostatic screening effect by surface charged impurities, graphene ripples (quenched flexural phonons), and resonant scatterers. The possibility of mobility enhancement by the screening of charged impurities on substrate surfaces by applying high ionic strength solutions or high dielectric constant liquids has been demonstrated recently with varying degrees of success. Chen et al. reported a significant improvement in the mobility of mechanically cleaved graphene exposed to high ionic strength solutions while Ponomarenko et al. reported no significant improvement for graphene placed on various substrates in high dielectric constant liquids.

Insights into the main limiting factors in carrier mobility can be obtained by studying the $I$–$V$ characteristics of a single-layer graphene film versus that of few-layer graphene film. According to our measurements (Figure 2b, Figure 2d, and Figure 2f), the carrier mobilities of the bilayer and trilayer graphene film are higher than that of the single-layer graphene film by $\sim 10$ times. This indicates that the main limiting factor is not sheet-to-sheet junction resistance but is dominated by other effects, i.e., impurity scattering from the SiO$_2$ substrates. Such impurity scattering effect will be expected to be more pronounced in single-layer graphene film compared to few-layer graphene film due to poorer screening in the former as a result of lower carrier concentration. Coulomb scattering is also expected to be dominant in devices where mobilities are low in the range of $\sim 100-1000$ cm$^2$/V·s. A verification of the impurity scattering effect can be seen when we exposed our CPG device to NaF electrolytes of different ionic concentrations to investigate the changes in transfer characteristics in back-gate configuration (Figure 4b). The ionic electrolyte provides the ionic screening needed to nullify the electric field from the charged impurities on SiO$_2$ substrate. Remarkably, an improvement by over 1 order of magnitude for hole and electron mobility (e.g., hole mobility increased from 365 to 5511 cm$^2$/V·s) and on/off ratio (by 10 times) (Figure 4c,d) can be achieved for the CPG device. This proves that the screening effect of the charged impurities on SiO$_2$ substrate is sufficient to screen charge impurities on the substrate. In addition, the Dirac point shifted toward zero gate voltage with increasing ionic strength of NaF, thus indicating the screening of electric fields created by charged impurities on SiO$_2$ substrate and the nullification of doping. The reduction of asymmetric factor is also evident from Figure 4c, which can be rationalized on the basis of the screening of Coulomb scatterers. Therefore, the main scattering mechanism that limits the mobility of ultrathin CMG-based device is attributed to Coulomb scattering. Figure 5 compares the field-effect mobility of transistor made from different reduced GOs. The best mobility value of 5000 cm$^2$/V·s is obtained from transistors with the source, channel, and drain made from reduced GO film and with the channel region subjected to ionic screening by 1 M NaF electrolyte.

In conclusion, we have demonstrated a strategy to fabricate high mobility chemically processed graphene films derived from large-sized graphene oxide sheets. A combination of several factors allows the attainment of unprecedented performance, which underpins the important influences of size effect in the GO, contact resistance, and impurity scattering. An all-carbon graphene FET device is shown to improve the charge carrier mobilities significantly. By ionic screening of the charged impurities, we obtained intrinsic carrier mobility greater than 5000 cm$^2$/V·s for our thin-film graphene device. This value, which is close to that of mechanically cleaved graphene ($\sim 10000$ cm$^2$/V·s), is 3 orders of magnitude higher than previously reported mobility values on chemically derived graphene films. The importance of this work shows that chemically processed graphene derived from large-sized GO maintains the intrinsic structural cohesion and two-dimensional delocalized $\pi$-electron network needed for a functional high mobility transistor. These results are exciting because they reaffirm the potential of solution-processed GO sheets for large scale printable all-carbon electronics.

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Supporting Information Available. Experimental details, optical micrograph and AFM images, size distribution of graphene flakes, electrical characterization of a single flake, and optical contrast spectroscopy. This material is available free of charge via the Internet at http://pubs.acs.org.
REFERENCES AND NOTES