

High-throughput solution processing of large-scale graphene

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The electronic properties of graphene, such as high charge carrier concentrations and mobilities, make it a promising candidate for next-generation nanoelectronic devices^{1–3}. In particular, electrons and holes can undergo ballistic transport on the sub-micrometre scale in graphene and do not suffer from the scale limitations of current MOSFET technologies^{2,3}. However, it is still difficult to produce single-layer samples of graphene^{1,3} and bulk processing has not yet been achieved, despite strenuous efforts to develop a scalable production method^{4,5}. Here, we report a versatile solution-based process for the large-scale production of single-layer chemically converted graphene over the entire area of a silicon/SiO₂ wafer. By dispersing graphite oxide paper in pure hydrazine we were able to remove oxygen functionalities and restore the planar geometry of the single sheets. The chemically converted graphene sheets that were produced have the largest area reported to date (up to 20 × 40 μm), making them far easier to process. Field-effect devices have been fabricated by conventional photolithography, displaying currents that are three orders of magnitude higher than previously reported for chemically produced graphene⁶. The size of these sheets enables a wide range of characterization techniques, including optical microscopy, scanning electron microscopy and atomic force microscopy, to be performed on the same specimen.

Single-layer samples of graphene are currently made either by a laborious drawing method¹ or through the high-temperature reduction of silicon carbide^{7,8}. In the drawing method, highly oriented pyrolytic graphite (HOPG) is repeatedly peeled using cellophane tape and deposited onto a silicon substrate. Yields for this method are extremely low and involve searching the substrates for single sheets among a myriad of multilayered flakes. Even when likely specimens are identified with an optical microscope, atomic force microscopy (AFM) and Raman techniques must be performed in order to provide conclusive evidence of their identity^{1,9,10}. Alternatively, the reduction of silicon carbide can be used to produce very small domains of single-layer samples; however, temperatures >1,100 °C are needed and producing large domains remains a challenge^{7,8,11}. High-temperature processing is also unlikely to be compatible with fabrication techniques used for most electronic applications. Hence, current methods of producing graphene samples have very low throughput and do not appear to be scalable up to wafer size.

An alternative method for creating single sheets starting from graphite oxide (GO) has been suggested^{12,13}. Graphite can be oxidized to produce GO and then exfoliated to create stable aqueous dispersions of individual sheets. After deposition, GO may be reduced to graphene either chemically or by means of thermal annealing^{6,13}. However, this method has drawbacks. First, many of the resulting sheets are found to be wrinkled or folded when examined by AFM. Second, cross-sectional step heights of more than 1 nm are often observed for a single sheet¹³,

which is much larger than the theoretical value of 0.34 nm found in graphite. This increased thickness may be attributed to unreduced surface hydroxyl and epoxide groups. Such functionalities are detrimental to the electrical properties of graphene. Third, aqueous dispersions are not ideal for deposition as the high surface tension of water leads to aggregation during the evaporation process. Finally, even if GO is perfectly deposited, reduction methods tend to neglect the area in direct contact with the substrate. Attempts have been made to complete the reduction stage in solution, but sheets tend to aggregate due to the attractive forces between layers and an overall decrease in hydrophilicity^{12,13}.

Here, we present a solution-based approach for producing large-scale, single-layer chemically converted graphene. Dispersing GO paper in pure hydrazine creates stable dispersions of hydrazinium graphene (HG) through the formation of counter-ions. These hydrazine colloids are readily deposited onto a variety of substrates, producing uniform films of single- and/or few-layer chemically converted graphene. Photographs of GO paper and HG are presented in Fig. 1a,b respectively, along with three-dimensional molecular models of GO before and after reduction. By controlling the concentration and composition of these dispersions, films of a desired morphology and surface coverage can be produced. This non-destructive method preserves the scalability of GO, ultimately forming reduced sheets much larger than those previously reported^{6,11–14}. This increase in size vastly reduces the effort necessary for electronic testing and renders characterization possible by a number of microscopic techniques. In fact, the scale of graphene produced allows one of the most comprehensive studies yet conducted on the characterization of chemically converted graphene.

The reduction of GO by hydrazine vapours is well known^{6,12,16–19}, but here GO films are dispersed directly into hydrazine. Bubbles rapidly form along the film surface due to the chemical reduction, which likely produces NO₂ and N₂ as byproducts. After several hours, no GO paper can be visually observed in the dispersion and bubbling subsides, indicating good dispersion and complete reduction, respectively. As an explanation for the new dispersions created, we suggest the formation of HG composed of a negatively charged, reduced graphene sheet surrounded by N₂H₄⁺ counter-ions. Hydrazinium compounds are known to readily disperse in hydrazine²⁰. The resultant dispersions are stable for months with little aggregation due to charge stabilization of counter-ion pairs. Stable aqueous dispersions have been reported by others¹⁶, but differ slightly in their composition. Under aqueous conditions and low concentrations of hydrazine and high pH, carboxylic acid groups retain their negative charge, allowing adjacent sheets to repel one another. In anhydrous hydrazine, a greater number of these carboxylic acids are likely reduced and the positive charge of their N₂H₄⁺ counter-ions becomes responsible for stabilization. The dispersions are similar in that both use hydrazine as the

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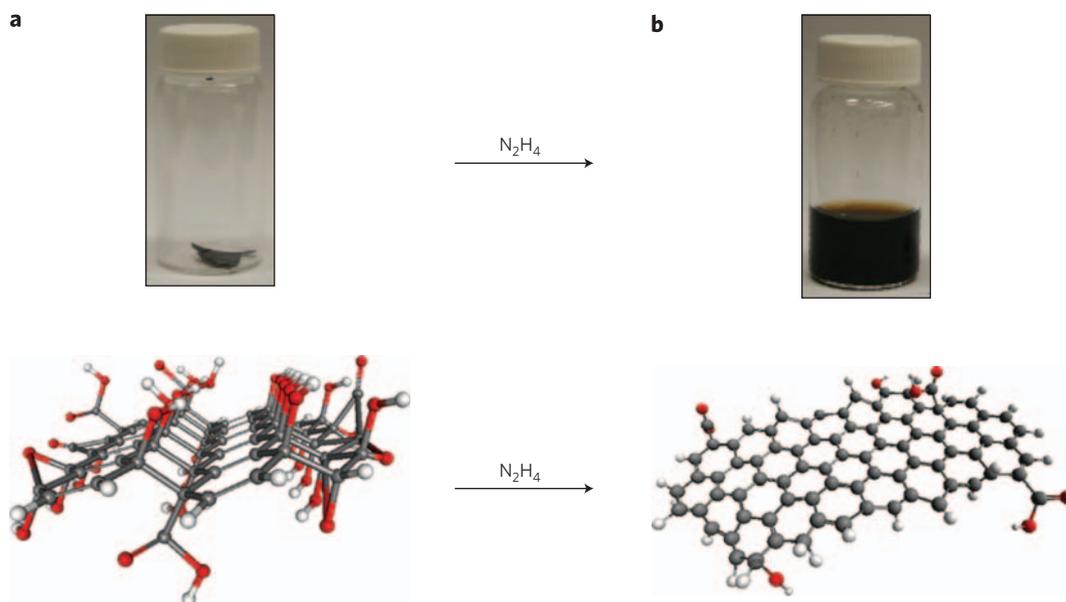


Figure 1 | Chemically converted graphene suspensions. a,b, Photographs of 15 mg of graphite oxide (GO) paper in a glass vial (a) and the resultant hydrazinium graphene (HG) dispersion after addition of hydrazine (b). Below each vial is a three-dimensional computer-generated molecular model of GO (carbon in grey, oxygen in red and hydrogen in white) and chemically converted graphene, respectively, suggesting that removal of $-OH$ and $-COOH$ functionalities upon reduction restores a planar structure.

reducing agent, but are quite independent due to the different solvent systems—water and pure hydrazine. Note that HG may be dried and resuspended in the organic solvents dimethyl sulphoxide (DMSO) or *N,N*-dimethyl formamide (DMF) for deposition, as has been reported for other hydrazinium complexes²⁰. This approach has the advantage of avoiding the requirement for spin-coating from a solvent of such toxicity as hydrazine.

Purification of HG solutions can be carried out with various combinations of ultrasonication, dilution and centrifugation. Briefly, dispersions of large ($20 \times 20 \mu\text{m}$) single sheets are created by precipitating out higher density multilayers by means of centrifugation. Such dispersions may be very useful for electronic applications due to the ease of making contact with the length scales of these relatively large single sheets. Alternatively, large sheets and aggregates may be fractured into uniform dispersions of smaller single sheets (for example, $1 \times 1 \mu\text{m}$) by repeated ultrasonication. These small sheets readily make continuous films upon deposition and may prove to be useful as ‘transparent’ conductors²¹. Note that even these smaller sheets are large when compared to those prepared by either the peeling method or by chemical reduction of SiC , which typically have dimensions areas of no more than $0.2 \mu\text{m}^2$.

The initial characterization of HG is carried out by spin-coating onto a silicon/ SiO_2 substrate and by examination through an optical microscope. Optical microscopy was originally used to identify single-layer, chemically converted graphene¹. Here, however, we use optical images primarily to observe the surface coverage of the depositions. For more detailed structural information, scanning electron microscopy (SEM) images were collected, with a representative image of a large single sheet ($\sim 20 \times 40 \mu\text{m}$) shown in Fig. 2. Under optimized operating conditions (see Methods), single, double and multilayer chemically converted graphene may be differentiated by opacity in SEM.

Although SEM images can be used to find single sheets of chemically converted graphene, the images are representative of electronic structure, not topography. Hence, AFM is needed to establish the thickness and surface roughness of single sheets. For comparison, a representative SEM and its corresponding AFM height images are shown in Fig. 3a,b, respectively. Height profiles show steps from

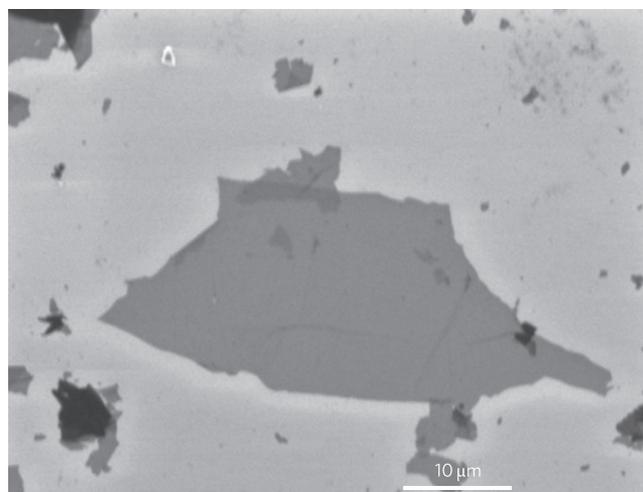


Figure 2 | SEM image of a large, single, chemically converted graphene sheet. Such sheets are readily identified in SEM on silicon/ SiO_2 substrates after spin-coating from hydrazine dispersions.

the SiO_2 to a chemically converted graphene sheet of $\sim 0.6 \text{ nm}$ for a given cross-section (Fig. 3d). Figure 3d shows the bimodal frequency distribution of all points recorded during an entire AFM scan, which also shows a peak separation of $\sim 0.6 \text{ nm}$. Exfoliated samples prepared by the annealing method in ultrahigh vacuum (UHV) also show typical step heights for single-layer exfoliated sheets of 0.6 nm (ref. 29). The apparent 0.3 nm discrepancy in thickness compared to theoretical values for graphene suggests the presence of some residual oxygen functionalities on the sheets²². Nevertheless, the agreement between peeled samples and those measured here provides significant evidence that the planar structure of graphene has been largely re-established upon reduction. Although reduced GO samples have been studied by AFM before,

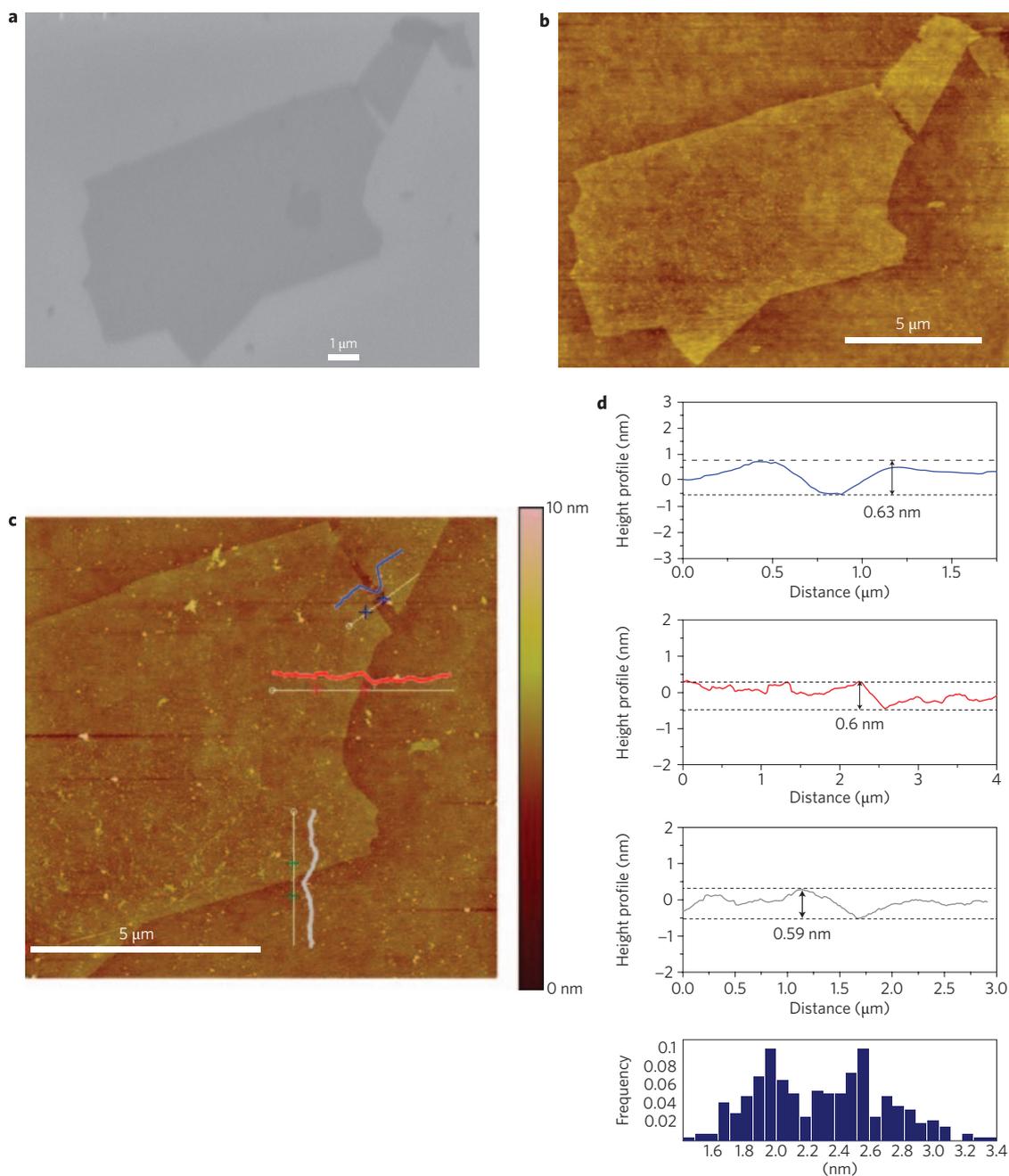


Figure 3 | Images of an individual chemically converted graphene sheet. **a–c**, Markers are used to obtain SEM (**a**) and AFM (**b,c**) images of the same specimen. **d**, Height profiles taken along the white, red and blue solid lines in **c** highlight step heights of ~ 0.6 nm. The frequency distribution (bottom) of all heights collected across the area is bimodal.

the size limitations of single sheets have not previously permitted such quantitative comparisons.

In an investigation of chemically converted graphene, the characterization of electrical properties and fabrication of electronic devices are of great importance. Owing to the size limitations of most graphene samples, electron-beam lithography has been the only reliable method for producing the patterns necessary for electrical testing. In a typical electron-beam process, single sheet candidates are located by SEM, markers provided, and a polymethyl methacrylate photoresist selectively exposed. After removing the photoresist, gold source and drain electrodes are then evaporated onto the surface to provide a top contact configuration for the graphene device. This method is laborious

and requires a sophisticated lithographic setup, making it difficult to scale up. Moreover, this lithographic process can degrade device performance by introducing contaminants if the photoresist is not entirely removed^{23,24}. The size of the chemically converted graphene sheets reported here, however, provides far fewer constraints for the effective fabrication of devices. The large sheets can instead be processed by means of conventional photolithography on SiO₂ substrates to provide gold source-drain top contacts. Figure 4 provides a schematic of our FET design (Fig. 4a) and a photograph, optical image, and SEM of a working device (Fig. 4b). Electrode separation channel lengths of 7 μm can be used and no alignment is necessary in order to reliably produce single-sheet devices. This is due to the nearly

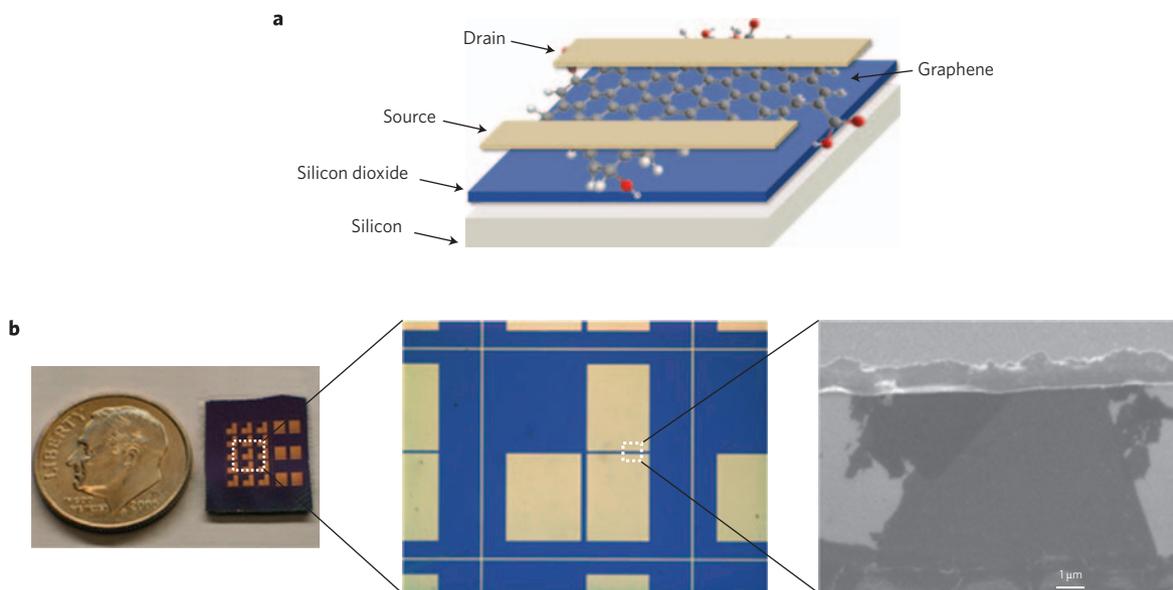


Figure 4 | Arrays of working, chemically converted graphene transistors. Field-effect transistors are produced by spin-coating a well-dispersed chemically converted graphene solution onto SiO_2 substrates, followed by registering gold source-drain electrodes on top of the single sheets. **a**, Schematic view of a chemically converted graphene field-effect device. **b**, Photograph (left), optical image (middle) and SEM image (right) of a working device with a channel length of $7 \mu\text{m}$.

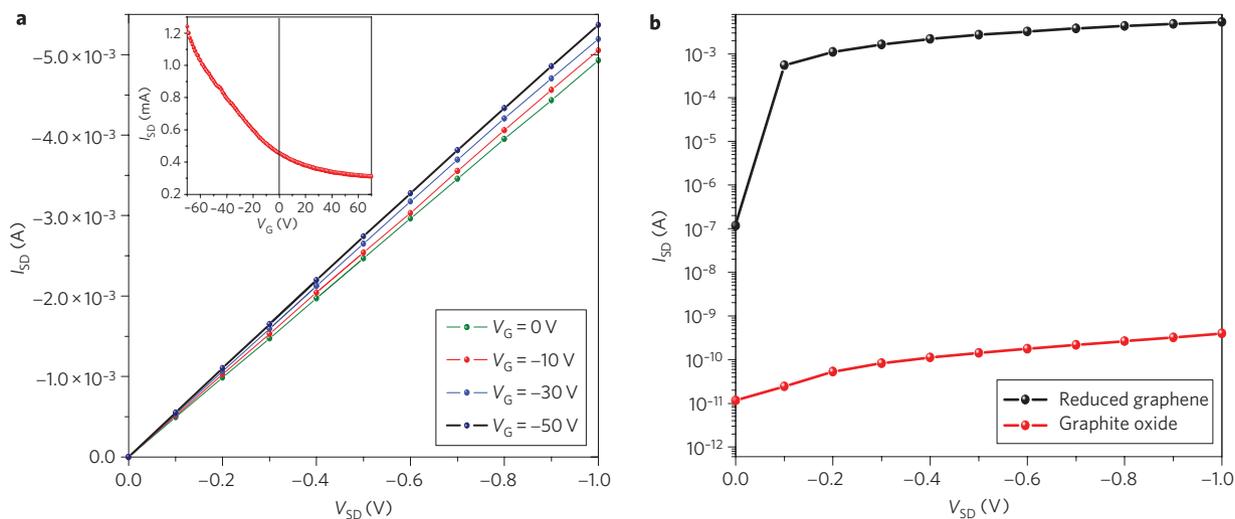


Figure 5 | Electrical characteristics of a chemically converted graphene field-effect transistor. **a**, Current (I_{SD})/voltage (V_{SD}) characteristics of chemically converted graphene devices. As the gate voltage is varied from 0 to -50 V , the conductance of the device increases, indicative of a p-type semiconductor under ambient conditions. The inset shows a $I_{\text{SD}}-V_{\text{G}}$ characteristic curve at $V_{\text{SD}} = 0.1 \text{ V}$. **b**, Current (I_{SD})/voltage (V_{SD}) plots taken for GO films before and after reduction indicate a 1×10^8 -fold decrease in sheet resistance.

uniform and tuneable distribution of single sheets over a large area of the wafer ($\sim 1.5 \times 1.5 \text{ cm}$).

More than 50 devices were tested to confirm the electrical output performance, with all measurements carried out under ambient conditions. p-Type behaviour is readily and reproducibly achieved at gate voltages ranging from 0 to -60 V . Figure 5a shows the output and transfer characteristics of a typical field-effect device. Output $V_{\text{SD}}/I_{\text{SD}}$ curves show more than 5 mA at source-drain voltages of only -1 V . This represents a considerable advantage over previously reported values for reduced GO ($25 \mu\text{A}$ at $V_{\text{SD}} = -5 \text{ V}$)⁶ at

considerably larger channel lengths ($7 \mu\text{m}$ versus 500 nm as previously reported). The results show current responses nearly comparable to those of graphene produced by the peeling method (up to $100 \mu\text{A}$ at $V_{\text{SD}} = 10 \text{ mV}$ and channel lengths of $0.5 \mu\text{m}$)¹. Figure 5b shows output curves for parent GO and our chemically converted graphene, indicating a 10^8 -fold decrease in resistance. We attribute the increase in conductivity to more complete reduction of GO by anhydrous hydrazine. Graphene samples produced using the drawing method should be understood to represent the ultimate reduction limit of our devices. We are, as of yet, unable to confirm

the ambipolar effect as obtained with peeled graphite under ambient conditions. Residual hydroxyl groups may inhibit n-type behaviour, as it is not observed at positive gate biases. Hydroxyl groups can serve as deep electron traps and prohibit their function as free carriers, as is well documented in silicon field-effect transistors^{6,11}. Several methods for the chemical modification of reduced samples to achieve n-type behaviour have been devised and are currently under investigation^{25–27}. These include functionalization, for example, alkylation, of parent GO materials before suspension in hydrazine.

The large size of the chemically converted graphene sheets produced here enable Raman spectroscopy to be carried out on a working FET. This provides a non-destructive method for characterizing graphene^{28–30}. D ($1,350\text{ cm}^{-1}$), G ($1,600\text{ cm}^{-1}$), 2D ($2,700\text{ cm}^{-1}$) and S3 ($2,950\text{ cm}^{-1}$) graphitic peaks are present in the spectra of the reduced samples. An increase of the D/G ratio upon reduction of GO is observed. Although a prominent D peak is typically an indication of disorder in the Raman of peeled graphene, our observations are consistent with previous reports of reduced GO¹². The strong D peak in chemically converted graphene should be further investigated, as presently it is somewhat paradoxical (see Supplementary Information for further discussion). If truly pristine, even chemically converted graphene should have a D peak only near the edges where sp^3 carbons are necessarily present.

In summary, the chemically modified GO materials presented here are the largest chemically converted graphene samples produced to date and can be readily processed in a reliable, scalable method. This technique is extremely versatile and can be used to create a myriad of coatings and geometries necessary for device applications and a full range of characterization techniques. We believe that the large scale of these single sheets represents a breakthrough in fabrication and could pave the way for new and innovative experiments on single-layer, chemically converted graphene.

Methods

Dispersions of GO were produced using a modified Hummers' method from graphite powder¹⁵. Typical dispersions were 2% wt/vol GO in water and could be diluted to various concentrations for use. Uniformity of a given dispersion was ensured by heating to $60\text{ }^\circ\text{C}$ with repeated ultrasonication. In order to form GO paper, aqueous samples were subjected to vacuum filtration through a $0.22\text{-}\mu\text{m}$ alumina membrane. This filtration process lasted $\sim 24\text{ h}$, after which the resultant films were left to dry under ambient conditions. Each dry, matte black GO film was then carefully peeled from its membrane.

For reduction and suspension as HG, 15 mg of the GO film was dispersed directly into a 98% anhydrous hydrazine solution (10 ml) in a nitrogen-filled dry box and allowed to stir for one week.

To begin characterization, HG suspensions were spin-coated onto silicon/SiO₂ substrates. Following deposition, the films were thermally annealed at $150\text{ }^\circ\text{C}$ in order to remove all hydrazine and to return the HG samples to chemically converted graphene.

SEM images were collected under a variety of accelerating voltages and probe currents in an attempt to improve contrast and resolution. Ultimately, a relatively small accelerating voltage (2–5 kV) and probe current (5–8 μA) proved most appropriate as they reduced the penetration depth of incident electrons and more directly probed surface species.

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Author contributions

V.C.T. and M.J.A. conceived and performed the experiments and measurements. Y.Y. and R.B.K. conceptualized and directed the research project. All authors discussed the results and contributed to the manuscript.

Additional information

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