Controlling the macroscopic electrical properties of reduced graphene oxide by nanoscale writing of electronic channels

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Abstract

The allure of all-carbon electronics stems from the spread of its physical properties across all its allotropes. The scheme also harbours unique challenges, such as tunability of band gap, variability of doping and defect control. Here, we explore the technique of scanning probe tip-induced nanoscale reduction of graphene oxide (GO), which nucleates conducting, sp² rich graphitic regions on the insulating GO background. The flexibility of direct writing is supplemented with control over the degree of reduction and tunability of band gap through macroscopic control parameters. The fabricated reduced GO channels and ensuing devices are investigated via spectroscopy and temperature and bias-dependent electrical transport and correlated with spatially resolved electronic properties, using surface potentiometry. The presence of carrier localization effects, induced by the phase-separated sp²/sp³ domains, and large local electric field fluctuations are reflected in the non-linear transport across the channels. Together, the results indicate a complex transport phenomenon, which may be variously dominated by tunnelling or variable range hopping or activated depending on the electronic state of the material.

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(Some figures may appear in colour only in the online journal)

Introduction

The realization of graphene-based electronic devices has been restricted primarily due to the lack of reproducible and cost-effective preparation techniques for graphene and the absence of an electronic band gap (Eg) [1]. Superficially, graphene oxide (GO) appears to offer a suitable alternative in terms of scalability following various modifications of the Hummer’s method [2] and also due to the presence of a notional band gap in its density of states (DOS). GO results from the addition of oxygen-containing side groups to the hexagonal carbon lattice of graphite via an acid functionalization process, and subsequently reducing some of these states with hydrogen, while passivating the defects. However, research into controlled defect incorporation into graphene [3–6] has shown that surface adsorbates or doping-induced band structure tailoring compromises the ensuing electrical properties and likewise in GO. Like graphene, GO has a layered structure but with significantly larger inter-planar separation.
due to incorporation of the epoxy groups, which makes it amenable to exfoliation. The incorporation of the oxygenated functional groups severely disrupts the honeycomb lattice of graphene, making GO a very dirty insulator with dubious electrical properties. In reverse, the reproducible reduction of GO to graphene has proved to be a non-trivial task. While it has been shown that more than 90\% of the oxygen-containing groups can be effectively removed from GO [7], the restoration of long-range $sp^2$ network and the associated electrical and optical properties, akin to those of graphene, remains challenging. Since the physical properties of this intermediate material, reduced GO (rGO) lie between those of GO and graphene, any systematic variation of rGO physical state and properties by controlled reduction is of huge fundamental and technological importance. Although innumerable chemical [8–10] and physical [11–16] reduction methods have been reported, the identification of robust and controllable process parameters remains elusive. From a more fundamental viewpoint, the atomic structure of rGO remains unclear, beyond the fact that the $sp^2$ network of graphene is disrupted in GO, creating a disordered lattice where the oxygen functional groups are covalently bonded to the carbon atoms along with some adsorbed oxidative debris. The process of structural rearrangement upon the reduction of GO to rGO and then graphene also remains hazy. Thermodynamically, GO would have higher entropy (disorder) compared to graphene (ordered), although energetically GO would be lower than graphene. As part of the reduction process, the oxygen functional groups, which are bonded with the $sp^3$ hybridized carbon atoms need to be removed from the system, allowing the amorphous carbon network to reorganize in the hexagonal lattice. The evolution of the electronic band structure of GO to rGO and then towards graphene, under progressive reduction, also remains unclear [17]. Angle-resolved photoemission spectroscopy of graphene, exposed to atomic oxygen does not display signatures of doping, unlike that for atomic nitrogen [18], but does evidence localization of electronic states in the valence band ($\nu_{\text{v}}$), especially those close to the Fermi level ($E_F$) [19]. This is similar to the case of atomic $N$ bonding to amorphous C, which has many non-doping states available via hybridized states [20]. Furthermore, the substrate is known to play a crucial role in determining the observed band structure of rGO, similar to the case of bilayer graphene, which has been shown to display a dispersionless flat band near the $K$ point along with a finite band gap [21]. The electrical properties of rGO, such as carrier density and mobility are also compromised compared to those of graphene with the best rGO samples exhibiting mobility $\sim 10^3 \text{cm}^2\text{V}^{-1}\text{s}^{-1}$, along with conductivity comparable to that of polycrystalline graphite [11]. Overall, investigations into the electrical and optical properties of rGO show wide variability, allowing multiple inferences to be drawn. Electrical transport in rGO has been variably shown to follow thermally activated transport [22] or 2D variable range hopping (VRH) [23, 24]. The latter may be dominated either by Mott-VRH or the electric-field-controlled Efros–Shklovskii (ES-VRH) model [25, 26]. Each of the above models is characterized by an exponent ($p$) describing the temperature ($T$) dependence of low-bias conductivity ($\sigma$), generically given as $\sigma(T) \propto \exp(-T_0/T)^p$, where $T_0$ is a fit parameter characterizing the material. The exponent $p$ assumes the value 1 for activated transport, and $1/3$ and $1/2$ for the 2D Mott-VRH and ES-VRH models, respectively. Based on temperature-dependent transport measurements alone, it is difficult to unequivocally distinguish between the two VRH models, often with data that may reasonably fit either model, in restricted temperature ranges. This ambiguity is not only restricted to rGO but extends to epitaxially grown monolayer graphene [27] and its amorphous counterpart, hydrogenated amorphous carbon (a-C:H) [28]. Theoretical calculations also show that scattering due to defect-induced charge impurities in graphene and the presence of localized states (near $E_F$) in rGO leads to spatial fluctuations in the surface charge density with local accumulation of electrons and holes, limiting the conductivity of the material [29].

Against this backdrop, we investigate a highly controllable and spatially accurate route to GO ‘reduction’ using a conducting atomic force microscope (C-AFM) based lithography technique that locally reduces GO to rGO [13, 14]. Here, repeated scanning of a designated area on monolayer to few-layer GO flakes, by a C-AFM tip under suitable bias and humidity, increases the local electrical conductance of the area, indicating the possible local reduction of GO. Scanning probe microscopy (SPM) based lithography techniques have been extensively researched over the last three decades [30, 31]. They offer integrated patterning and imaging capabilities, with high spatial resolution, depth of field and operational flexibility, i.e. a wide range of processable materials [30, 31] that are not possible with other techniques. In all cases, the scanning tip induces physical (mechanical, thermal, diffusive, etc) or chemical (oxidation, etc) changes to the surface, altering the local properties. The spatial resolution of these changes is dependent on the characteristic length scales of the interaction(s) exploited. In the present context, this is one technique that allows a single-step patterning cum reduction protocol and possible route towards realizing all-carbon electronic devices [32, 33]. Importantly, it decreases the use of lithography resists on 2D materials such as graphene, which are known to be sensitive to chemical organic residues. Although the technique has limited throughput, in its present form, it allows a high degree of control on the reduction process through a few highly controllable macroscopic parameters such as tip-sample bias ($\nu_{\text{v}}$), relative humidity ($RH\%$) and number of area scans or voltage cycles. Furthermore, the throughput limitations will be mitigated by the promise of scan speeds approaching millimetres per second, opening up newer avenues for tip-based material engineering and lithography.

There have been a few reports on C-AFM tip-based local reduction of GO, adopting thermal and electrochemical approaches to local modification of the GO surface [13–16]. While all these studies have been led by the basic aim of customizable and spatially localized nanometre-scale transformation of GO into rGO, the chemical identity and electronic structure of the resulting rGO has largely remained unexplored. In all cases, the primary indicator of ‘reduction’ has been change in local electrical property of the scanned
region, with the limited size of the modified regions restricting spectroscopic quantification of their chemical identity. Here, we continue to refer to these modified regions as rGO and investigate their chemical and physical properties, and importantly, the dependency of these properties on the macroscopic control parameters identified earlier. Although the exact mechanism of this tip-induced modification is still not fully understood, it has been proposed that desorption of oxygenated functional groups from the GO surface is induced by local electrochemistry in the presence of the tip-sample junction electric field [13, 14] and water condensed therein or thermochemistry [15, 16]. Apart from a significant increase in the local conductivity of tip-induced rGO (~10^3 S m^-1), which is comparable to that obtained by chemical reduction [16], little is known about its atomic/electronic structure and hence the carrier transport mechanism, which is investigated here. Available Raman spectroscopy studies over these tip-induced rGO domains have shown a relative increase in the fraction of sp^2 and sp^3 domains and reveal spatial inhomogeneity in the atomic structure [13, 14, 34]. Generically, the presence of this spatial inhomogeneity often leads to inhomogeneous electronic properties and as is expected in the case of the rGO proposed here. Along with change in topographic and mechanical properties of rGO, we have investigated the effect of reduction through recording the spatial inhomogeneity in local current and local conductance (dI/dV) of the surface. rGO devices fabricated by ‘drawing’ a conducting rGO channel between a pair of source–drain electrodes then allowed us to correlate the non-equilibrium, electrical transport properties of the rGO channel with the nanoscale electronic properties of the channel. The evolution of spatially resolved surface potential (V_S) maps under zero and non-zero source–drain bias reflects the variation in local electronic structure and quantifies the fluctuations in the local electric field, which are two orders in magnitude larger than the macroscopic field. Our results support the hypothesis that the observed non-linearity in the device current–voltage (IV) characteristics stems from intrinsic material inhomogeneity of the channel and the ensuing charge transfer between localized states, rather than purely from the metal-rGO contacts at either end of the device. The IV nonlinearities decrease systematically with the degree of reduction of the rGO channel, further justifying its origin based on the intrinsic material property that evolves with reduction. The rGO surface inhomogeneities are also visualized by 2D differential voltage (∇^2V_S) maps that evidence charge puddles extending over tens of nanometres. Overall, we present a combination of macroscopic and nanoscale electrical investigations characterizing the physical properties of rGO devices directly written (reduced) by a C-AFM tip together with micro-Raman maps characterizing the chemical nature of rGO.

**Experimental methods**

A water dispersion of GO (2.5 wt% concentration) sample was purchased from Graphenea. The suspension was further diluted in a 1: 20 volumetric ratio and then spin coated onto selected substrates for further processing and characterization. All AFM experiments were performed using the Bruker Multimode-8 AFM in a humidity-controlled environment. Experiments in the local reduction of GO were conducted by using the C-AFM mode equipped with a TUNA-2 module, capable of measuring junction current in the range of 1 μA–1 fA. The reduction was performed by applying a negative bias (typically between −2 to −5 V) to the substrate while keeping the conducting probe at virtual ground. Change in the local electrical property was measured by recording the current map and local conductance (dI/dV)|_Vdc map (CMAP) simultaneously with the topography under low dc bias (typically 100 mV). The dI/dV|_Vdc maps were recorded by modulating the applied dc bias (Vdc) with an ac bias (Vac < 5%) of Vdc) using a signal generator. All CMAPs were recorded with Vac = 100 mV, unless otherwise mentioned, by detecting the in-phase ac output voltage (≡ ac current signal) using a lock-in amplifier [35]. C-AFM experiments were conducted with Mikromasch Cr-Au coated conducting probes (HQ: CSC37) having force constant 1–2 N m^-1, while the tapping mode experiments were performed with NT-MDT NSG-30 probes having resonance frequency in the range of 240–440 kHz and stiffness of 40 N m^-1. Nanoscale surface potential mapping was undertaken using an Asylum Research MFP—Infinity AFM in the Kelvin probe force microscopy (KPFM) mode, which allows the measurement of surface potential through a two-pass operation. For KPFM measurements, Pt-Ir-coated Si tips (Nanosensors PPP-EFM) with stiffness of 2.8 N m^-1 and resonance frequency ~75 kHz were used. Lateral bias was applied in the tapping mode for potential mapping across the reduced GO region. The Raman spectroscopy measurements were conducted using a HORIBA XPLORA PLUS micro-Raman set up. Raman mapping was performed with a spatial resolution of 0.7 μm using 532 nm excitation (0.6 mW power) through a 100X objective with NA = 0.9 resulting in an illumination spot size ~720 nm. Temperature-dependent transport studies were conducted using a closed-cycle cryostat (ARS Inc.) interfaced with a custom-written LabVIEW programme controlling a Keithley 2400 source meter and Lake Shore 336 temperature controller.

**Results and discussion**

Figure 1(a) shows an optical image of the GO device electrode layout with the GO layer demarcated by a dashed line. Figure 1(b) shows AFM topography of the device before the reduction of GO along with a line scan across the edge of the GO flake indicating a monolayer with an average thickness of 1.78 nm. Figure 1(c) shows a schematic of the AFM tip-based nanoscale writing configuration and architecture of a three-terminal device. The surface colour map denotes experimentally recorded variation in local conductance of the GO flake. The initial tip-based reduction experiments were conducted with the GO flakes deposited onto conducting substrates (Au or ITO) with an optimal sample bias. Repeated reduction of GO flakes evidenced stable, uniform and
controlled reduction under negative sample bias around $-3\,\text{V}$, which was used as a standard through the study. Figure 2(a) shows a $2\,\mu\text{m} \times 2\,\mu\text{m}$ 3D height image of a rGO/GO film overlaid with the current map recorded at $-100\,\text{mV}$ dc bias, showing the variation in local current of 0 to $-1.9\,\text{nA}$ between the GO and rGO region ($500\,\text{nm} \times 500\,\text{nm}$ at the centre). The large current carried by the reduced region provides an indication of the change in local electrical property of the rGO region. Evolution of the local electrical properties was further investigated by recording of sequential point $\text{IV}_\text{s}$ across a junction, as a function of voltage cycles obtained by ramping the sample bias at $\pm 3\,\text{V}$, as shown in figure 2(b). Figure 2(c) shows the bias dependence of junction conductance ($G = dI/dV$) obtained by numerical differentiation of selected $\text{IV}_\text{s}$. The zero-bias conductance ($G_0$) gives a good measure of the change in local electrical properties with the number of cycles of bias ramps, as plotted in figure 2(d) for three different samples evidencing the systematic increase in $G_0$ with repeated bias cycles. The absence of measurable current in the first few bias cycles and the absence of any non-zero current (and thus $G$) at $\pm 1\,\text{V}$ in figure 2(c) attests to the insulating nature of the virgin GO flake, even though it rests on a conducting substrate. Figure 2(d) also indicates that while the rate of increase of $G_0$ (degree of reduction) with bias cycles increases rapidly between the 5th and 50th cycle, it slows down in subsequent cycles with $G_0$ "saturating" thereafter. Together, the $\text{IV}$ characteristics and $GV$ plots demonstrate an increase in local conductance by over four orders of magnitude between the 5th and 100th bias cycles, at a single point. The above behaviour is highly reproducible across multiple GO samples, as shown in supplementary figure 1, (available online at stacks.iop.org/NANO/32/175202/mmedia).

Tip-induced nanoscale anodic oxidation is a well-known nanolithography technique applied to metals, semiconductors and even graphene [30, 31, 36]. Here, the key role is played by the presence of a water bridge formed in the nanoscale tip-sample junction of an SPM, due to capillary condensation [31, 37, 38] under ambient conditions. It has been suggested that the high electric field at these biased junctions facilitates the formation of a water bridge and play a dominant role in the reduction of GO [14, 31, 39]. Our investigation into the effect of environmental humidity on the tip-assisted GO reduction showed that higher relative humidity (RH) favours reduction. Supplementary figures 2(a) and (b) in the supplementary material show the variation in local current and conductance ($dI/dV$) map across different regions reduced with RH that varied between 20%−80% on GO. Below RH of 20%, no reproducible change in local electrical properties was observed even for sample bias $-5\,\text{V}$ and repeated cycles of reduction. All results presented subsequently have been recorded with RH at 55 ± 5%. The local electrical properties of these rGO regions remain unaltered even after a few months after reduction (see supplementary section SI-3B). These initial results together indicate that the GO reduction process discussed here, as quantified by the change in local electrical properties, is determined by the following experimental control parameters, sample bias, RH and time, the latter quantified by the number of reduction cycles. Tip-induced reduction of GO not only allows spatial confinement of reduction over customizable patterns, but a degree of control over tuning the conductance of the rGO region by controlling the above three parameters. The process has significant implications in nano/microscale device fabrication [30].

Having standardized the reduction protocol in terms of the aforementioned control parameters, GO flakes were immobilized on insulating 300 nm SiO$_2$ on $p$-doped Si substrates and subsequently contacted with electrical pads, as shown in figures 1(a) and (b). Connecting the two electrodes in the source–drain configuration, an rGO channel was patterned by repeatedly scanning the tip over the designated area, as shown in figure 1(c). During the process, the two electrodes were shorted and connected to $-3\,\text{V}$ bias used for reduction. Figure 3(a) shows the conductance map recorded in the device area, clearly demarcating the source–drain electrodes and the interconnecting conducting channel of rGO. The $dI/dV$ map shows that the reduction process induces an increase in average local conductivity by a factor of 10 after five reduction scans, which is reproducible keeping
the macroscopic experimental parameters fixed. However, some variation in conductivity change has been observed based on the quality of the immobilized GO flake, which is difficult to quantify. Although the change in the electrical properties between the ‘reduced’ and virgin GO regions is quantifiable and directly evident, delineating the chemical identity of the regions remains unclear. The pathway to the defect formation also matters in the electronic conduction adopted by the defect state [40]. If the higher conducting regions are indeed rGO, then their chemical identity would necessarily be different to that of GO. Some indication of the change in this chemical identity of the ‘reduced’ region is obtained from the AFM tapping mode phase image shown in figure 3(d), which evidences a distinct contrast between the region that had been repeatedly scanned under high negative bias and the ‘un-scanned’ GO region. This gives the first direct indication of change in material property or chemical identity of the ‘reduced’ region vis-à-vis GO [41, 42]. GO is electrically insulating in nature due to significant disruption of the $sp^2$ network of graphene, upon incorporation of the various oxidizing groups and consequently, the carbon atoms in a GO layer would show amorphous or disordered arrangement along with interspersed $sp^2$ and $sp^3$ domains [43, 44], as shown in figure 4(a). The absence of long-range order in GO and its insulating nature nominally confirms the absence of $sp^2$ domains or if locally present they do not form a percolating network across the GO surface. Generically, the reduction of GO to rGO would remove the oxidizing groups and increasingly restore the $sp^2$ network [43, 45] by local nucleation of C=C bonds and restoration of six-fold C rings, as shown in figures 4(b) and (c). For the tip-induced reduction, the junction electric field in the presence of the water bridge likely leads to local ‘removal’ of the oxygenated functional groups [46] and is accompanied by delocalization of the associated electron cloud, albeit only over the reduced region and with increasing local conductance. At this stage, it remains unclear whether ‘removal’ results in complete desorption of the offending functional groups from the surface or
possibly their surface migration/diffusion away from the scanned region, under the action of the junction field, etc. To estimate this extent of local nucleation of C\(_=\)C bonds and C rings, micro-Raman spectroscopy and mapping was employed [47–49]. Evolving signatures of both C\(_=\)C \(sp^2\) hybridized carbon and the C rings offer the first indicators towards the restoration of the hexagonal network of graphene (figure 4(d)). Figure 3(c) shows the optical image of a two-terminal monolayer GO device, with the red rectangle indicating the reduced region and the green rectangle denoting our area of interest corresponding to the data presented in figure 3(d). The Raman spectra acquired at two spots each in the ‘reduced’ and pristine GO regions are shown in figure 3(e). All the spectra are normalized with their respective intensity \(I_D\) at the D-band peak (~1330 cm\(^{-1}\)). Spectra prior to normalization are shown in the inset. The normalized spectra show that the G-band (~1580 cm\(^{-1}\)) intensity \(I_G\) is relatively weaker, compared to the D-band intensity, for spectra recorded on the ‘reduced region’ than on pristine GO. This is more clearly shown in the series of images in figure 3(d), which plots the spatially resolved conductance map and \(I_D/I_G\) ratio along with the FWHM of the G \(\Gamma_G\) and D \(\Gamma_D\) bands, acquired within the green rectangle in figure 3(c). The D and G peaks are well-known Raman signatures corresponding to the in-plane stretching of \(sp^2\) C\(_=\)C bonds and symmetric breathing of standalone six-fold C rings, respectively. The latter also quantifies the degree of order/disorder within an agglomeration of C atoms [50, 51].

Assuming the arrangement of carbon atoms in the native GO to be highly disordered (see discussion on Raman line-widths below), the tip-induced reduction process would

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**Figure 3.** Correlating spatially resolved conductance and Raman maps across GO-rGO regions. (a) Conductance map of the rGO device. Scale bar: 2 \(\mu\)m. (b) Optical image of the device. Green box shows the area of interest and magenta box shows approximate boundary of the reduced region. (c) Normalized Raman spectra at various spots over ‘reduced’ GO and pristine GO regions. Inset shows the same spectra prior to normalization. (d) Spatial maps in the area of interest showing phase and conductance \((dI/dV)\) contrast, \(I_D/I_G\) ratio and \(\Gamma_G\) and \(\Gamma_D\) between the rGO region in the middle and GO regions on either side. Vertical dashed lines indicate boundary of the scanned region. (e) Averaged line scan across the \(I_D/I_G\) ratio and \(\Gamma_G\) and \(\Gamma_D\) maps in (d).
increase local order leading to the formation of graphitic domains, increase in-plane electrical conductance above a critical fraction and overall size of the graphitic domains (see figure 4(d)). The $dI/dV$ map in figure 3(d) shows a clear contrast between the pristine GO and reduced rGO region as do the $I_D/I_G$, $\Gamma_D$ and $\Gamma_G$ maps with a high degree of spatial registry across the four maps. Line scans taken along the length $I_D/I_G$, $\Gamma_D$ and $\Gamma_G$ maps (and averaged across their width) are shown in figure 3(f). While the $I_D/I_G$ value on native GO varies between 0.99–1, the tip-modified section (rGO) shows an increased value in the range of 1.14–1.17. The $I_D/I_G$ ratio has been used earlier to quantify defects and disorder in graphene and other related carbon networks [47, 48, 50]. While an increase in $I_D/I_G$ ratio in crystalline graphene quantifies an increase in defect density (disorder), the opposite may be concluded for dominantly amorphous carbon systems such as GO, where an increase in $I_D/I_G$ ratio denotes the restoration of aromatic six-fold C rings [50], signature of reducing defects and increasing order. Here, the increase in the value of $I_D/I_G$ in the reduced region likely indicates the increased formation of C rings. The increased magnitude of $I_D/I_G$ from 0.99 for GO to 1.17 for rGO, may also be used to estimate a disorder parameter, i.e., mean distance between the defects, which increases by $\sim 10\%$ [48].

Further confirmation of increased order in the reduced region is obtained from the narrowing of the D and G peak widths shown by the $\Gamma_D$ and $\Gamma_G$ maps (figure 3(d)) and line scans (figure 3(e)). The large values of $\Gamma_D$ ($\sim 90$ cm$^{-1}$) and $\Gamma_G$ ($\sim 60$ cm$^{-1}$) obtained for the GO samples demonstrates the highly disordered or amorphous nature of the starting material. At the reduced region, $\Gamma_D$ decreases by $\sim 20$ cm$^{-1}$ and $\Gamma_G$ decreases by $\sim 10$ cm$^{-1}$. The D and G peak width depends on the phonon lifetime, which in turn depends on the size of $sp^2$ domains. The decreasing peak width also indicates increasing lifetime ($\Gamma \propto 1/\tau$), which would be indicative of reduced scattering probability from defects [52]. Altogether, the decrease in the parameters $\Gamma_D$ and $\Gamma_G$, increase in the $I_D/I_G$ ratio coupled with the increase in local conductance of the reduced regions show increase in order, i.e. hexagonal $sp^2$ C rings and also indicate increase in $sp^2$ domain size with decreasing interdomain separation [53].

The envisaged atomic model of rGO, i.e. phase-separated regions of graphitic domains, hexagonal C rings, etc, embedded within the amorphous carbon background would create a system with highly heterogeneous surface electrical properties. With increasing reduction, higher conductive graphitic regions would increase in size and density [40] at the cost of the disordered carbon background, ultimately giving rise to long-range hexagonal order, as depicted in figure 4. The associated surface inhomogeneity and its role in mediating the lateral electrical transport was probed using scanning KPFM, a surface potentiometry technique, which allows accurate spatial profiling of surface potential. The KPFM measurements rely on the matching of tip bias ($V_{BC}$) with the contact potential difference between the sample and probe, $V_{CPD}$, by nullifying the vibration of the probe, which is initially driven by the electrostatic force, induced on the AFM probe. We note here that the mapped surface potential in KPFM has contributions arising from differences in work function between tip and sample, as well as the presence of uncompensated surface charges (particularly for non-metallic samples) [54, 55]. We reiterate that the rGO devices investigated here were fabricated on GO flakes immobilized between two pre-patterned Au probes on 300 nm SiO$_2$ on Si (p$^{++}$). As shown in figure 5(a), the conducting Si substrate and one Au contact were grounded with lateral dc bias ($V_L$) applied to the other Au contact. Figure 5(b) shows the surface potential ($V_s$) variation across a typical rGO channel, in the absence of any externally applied $V_L$ ($=0$), the colour bar showing a potential range of $\sim 60$ mV. Figure 5(c) shows the surface potential map of the rGO channel for various $V_L$ between 0–1 V. All the 3D plots have been shown with a fixed vertical axis range but with the colour map range varying with $V_L$ for clarity (see figure caption). As expected, all potential maps for non-zero $V_L$ show linear potential variation along the direction of the applied potential ($x$), i.e. length of the rGO channel. Note that at the source and drain electrodes, where the rGO channel is in contact with the
map corresponding to \( V_L = 0 \) V with \( \Delta V_s \) range \( \sim 60 \) mV reflects the spatial variation of the tip—surface contact potential difference (\( V_{CPD} \)). The \( V_{CPD} \) for metal-metal junctions quantifies the difference between the work functions of the tip and sample. The same interpretation may be extended to a junction between a metal tip (Au) and gapped semiconductor or semi-metal sample (rGO). Here, the sample work function (\( \phi_s \)) is given by \( \phi_s = E_C + \chi - E_F - eV_B \) [56], where \( E_C \) is the conduction band minimum, \( E_F \) is the Fermi level, \( \chi \) is the electron affinity and \( eV_B \) quantifies any band-bending due to surface effects, such as charges, unsaturated bonds, etc.

Thus, the zero-bias potential map in figure 5(b) indicates that the GO region has a higher \( V_{CPD} \) with respect to the tip (Pt) \( E_F \), which is held at 0 V (virtual ground), compared to the rGO region. The \( V_{CPD} \) difference arising from a difference in the \( \chi \) and \( eV_B \) between GO and rGO regions. This experimental finding is qualitatively commensurate with the equilibrium band diagrams at the GO-rGO interface, where GO has a larger band gap compared to rGO, but this does not allow us to extract values for the individual band gaps. In interpreting the contrast in the potential maps (figure 5(c)), we assume that these rGO channels form a composite 2D heterostructure. Where the disordered GO background, modelled as a bandgap semiconductor, embedded with more conducting and ordered graphitic domains, akin to the schematic shown in figures 4(b) and (c) constitutes the rGO [24, 34]. Thus, the rGO surface is a composite, composed of materials with spatially varying band properties and doping, nucleating a 2D array of nanoscale junctions at the domain boundaries. Indeed, it can be shown that the spatial contrast of the potential map would be theoretically given by

\[
\delta V_s(x, y) = \delta E_C(x, y) + \delta \chi(x, y) - e\delta V_B(x, y)
\]

For the \( V_L = 0 \) V case, thermodynamic equilibrium across the rGO surface, i.e. a spatially invariant \( E_F \), is established by charge transfer and band-bending across the domain boundaries giving rise to the local potential variation, strong boundary electric fields and localized charges. Figure 6(a) shows the quiver plot of the local electric field, calculated for a section of the potential map for \( V_L = 0 \) V. The direction and strength of the electric field is represented by the orientation and length of the arrows. The stronger fields localized at the domain boundaries demarcate the dominant scattering as would impede electrical transport along the rGO channel. Figure 6(b) shows the potential map and quiver plot for \( V_L = +1 \) V (applied to the right electrode keeping the left electrode at ground potential), showing a dominantly linear potential drop along the length of the channel with the local fields primarily pointing along the negative x-direction. Figure 6(c) again plots the surface potential for \( V_L = +1 \) V, but after subtraction of the local dc potential, i.e. linear plane corrected, and the corresponding local electric field.

The sample corresponding to the data shown in figures 5 and 6 had an rGO channel length of 11.5 \( \mu \)m and width 2.5 \( \mu \)m. For the \( V_L = 1 \) V, the measured \( \Delta V_{CPD} \) between the source–drain electrodes was 550 mV, which corresponds to a macroscopic dc electric field of \( 4.1 \times 10^4 \) V m\(^{-1}\) along the channel. By comparison, the local fields obtained from the underlying Au electrode, \( V_S \) shows no variation along the x-direction. Between the electrodes, the rGO channel assumes a potential commensurate with the applied \( V_L \). The difference between the applied \( V_L \) and measured \( V_S \) likely originates from a contact resistance within the electrical circuit. The \( V_S \)
Experimental potential maps have a wide distribution in magnitude, varying between $10^{-10} \text{ V m}^{-2}$ and $10^{-1} \text{ V m}^{-1}$, with a mean value of $\sim 4.3 \times 10^{-4} \text{ V m}^{-1}$, close to the calculated macroscopic field. The large difference between the macroscopic and microscopic field values likely plays a dominant role in determining the nature of electrical transport in these systems and explains the observed variation in the VRH transport presented in earlier reports [24, 27].

Higher spatial inhomogeneities in the potential map would correspond to both higher local fields and spatial non-uniformity with respect to the macroscopic mean value. The measured surface potential $V_S(x, y)$ would satisfy the Poisson equation given by $\nabla^2 V_S(\vec{r}) = -\rho(\vec{r})$ where $\epsilon(\vec{r})$ is the spatially dependent permittivity and $\rho(\vec{r})$ is the local charge density. A few-layer rGO sample would have a highly anisotropic and inhomogeneous permittivity, which is rather difficult to properly account for in the mathematical model to calculate $\rho(\vec{r})$. However, even neglecting the spatial dependence of $\epsilon(\vec{r})$, the 2D surface plot of the quantity $\nabla^2 V_S$ provides useful information regarding localization of charges on the rGO surface and their associated length scales. Figures 6(d) and (e) show the $\nabla^2 V_S$ plots for the case of $V_L = 0$ and 1 V, corresponding to those shown in figures 6(a) and (b). The images for the $V_L = 0$ V case show that $\nabla^2 V_S$ changes sign (signifying local positive and negative charges) over length scales of 80–100 nm, which is similar to that seen for the case of $V_L = 1$ V. Significantly, the rms surface roughness of the plots decreases from $2.96 \times 10^{11} \text{ V m}^{-2}$ to $2.12 \times 10^{11} \text{ V m}^{-2}$ between 0–1 V bias. Thus, the drift-diffusion current resulting from application of the external bias decreases the surface roughness—in effect ‘smoothening’ the charged surface and thus reducing scattering and decreasing

**Figure 6.** Spatial inhomogeneity of the surface potential, electric field and charge across an rGO surface. Spatial maps of local surface potential ($V_S$) for a section of rGO channel. Arrows indicate local electric field for (a) 0 V applied across the channel; (b) +1 V applied to the right electrode, left electrode is at zero; (c) same as (b) after subtraction of the linear potential gradient. Direction and length of arrows represent the direction and relative strength of local electric field. Colour bar shows variation of $V_S$ in mV. (d) and (e) show mapping of $\nabla^2 V_S$ for 0 V and +1 V applied external bias between two electrodes, respectively. Unit of $\nabla^2 V_S$ represented by colour bar is V m$^{-2}$; Scale bar: 1 μm.
channel resistance at higher bias (see discussion on IV data below). As mentioned earlier, the spectral features of the D and G peaks obtained in the Raman spectra of rGO and graphene provide information on spatial defect distribution [47] and graphitic domain size in the system. Previous investigations on chemically reduced rGO have reported typical $I_D/I_G$ ratios in the range 1–2 corresponding to graphitic domain sizes less than 10 nm [7, 57], which is also corroborated in atomically resolved topographic data [34] and electrical transport measurements [23]. The present case for rGO with $I_D/I_G \sim 1.17$ (figure 3(c)) would likely yield a similar estimate for the localization length scale, which is in contrast to the fluctuation length scales seen in the $\nabla^2 V_i$ plots above. However, these ‘charge puddles’, with lateral extent over tens of nanometres have been reported in graphene [5, 58–60], rGO$^5$ and Dirac semi-metals [61, 62] in which charge impurities arising from surface adsorbates, substrate and defects lead to large spatial charge fluctuations, especially with $E_F$ close to the Dirac point. The spatial extent of the observed charge puddles are primarily decided by two factors, background permittivity and free carrier density, which together determine the lateral screening length ($\xi$). The typical carrier density in rGO may vary between $10^9$–$10^{12}$/cm$^3$ [32, 63] with a wide variation in relative permittivity observed between 3–1000 [64–66], even influenced by environmental conditions. Both these parameters are also spatially variable on the inhomogeneous rGO surface and strongly influenced by the substrate and environment [29, 58, 60]. Thus, even though the disordered domains (harbouring the charged impurities) may be localized over a few nanometres, the resulting charge localization or screening distance may extend over significantly larger length scales, as can be seen here.

As mentioned earlier, repeated scanning of the rGO channel by the C-AFM tip (at fixed $-3$–$3$ V sample bias) increases the local conductance within the channel and also increases the overall lateral conductance of the channel, finally saturating to a steady-state value. Typically, it was possible to increase the lateral channel conductance by $\sim 10^4$ times by repeatedly scanning the same area more than 60 times, reaching a steady-state value. Experimentally, a larger number of reduction scans results in physical damage to the rGO layers and hence should be avoided. Figure 7(a) shows the semi-log plot of lateral IV characteristics obtained for the device, where the designated area between the source–drain contacts was repeatedly scanned with the C-AFM tip under $-3$ V tip-sample bias for the reduction of GO. The nonlinear IVs are representative of electrical transport through highly disordered systems, where tunnelling and/or hopping between localized states or spatially segregated electron-rich domains (figures 4(b) and (c)) gives rise to channel conductance. Electrical transport in rGO has been previously reported to be described by various 2D-VRH models [24, 63] as well as thermally activated transport [22, 63], similar to experimental observations in graphene [6, 27, 67]. There is limited understanding about the exact physical parameters that bring about each of the transport mechanisms, their domain of applicability and importantly the consequences of such identification of transport model. Figure 7(a) also indicates that the channel conductance ($G$) systematically evolves with progressive reduction cycles—quantified by the number of tip scans performed. Figure 7(b) shows that the zero-bias conductance $G_0$ increased by three orders of magnitude between the 16th–70th scan, which is the typical evolution observed across the various devices investigated. Along with the increase in $G_0$, the bias-dependent non-linearity decreases significantly with the increasing number of scans. The normalized dynamic conductance at 1 V, i.e. $G(1 V)/G_0$ (figure 7(b) right axis plot) decreases from 2.3 (16th scan) to 1.2 for the 58th scan and indicates progression towards linear or increasingly ohmic transport along the channel. To analyze the evolution of electrical transport along the channel with reduction, we obtained the conductance spectra, $G = dI/dV$ versus $V$, by numerically differentiating the IV characteristics, which were fitted to an empirical formula given by,

$$ G(V) = G_0 \left( 1 + \left| \frac{V}{V_0} \right|^n \right). $$

where $V_0$ and $n$ are fit parameters. Figure 7(c) plots $\ln(G/G_0 - 1)$ versus $\ln(V)$ for the IV's recorded after the 16th, 34th and 58th scans, where the slope and intercept yield the parameters $V_0$ and $n$ of the equation above. Evidently, a single exponent does not fit the entire bias range and in all cases shows a distinct cross-over, demarcating high- and low-bias regimes. The linear fits in these regimes show that $n \sim 1 (\pm 0.2)$ for the high-bias regime and $n \sim 4 (\pm 0.5)$ at lower biases, across all IV's studied. The bias dependence also indicates that close to zero bias the conductance has a significantly stronger bias dependence than in the high-bias regime. In all cases, the final device has the lowest resistance. However, even the most conducting device still exhibits non-linear conduction, resulting in significantly lower device resistance at higher bias ($\geq 1$ V). This is consistent with the decrease in rms roughness of the $\nabla^2 V$ surface plots between 0–1 V seen earlier. It is worth reiterating that the GO flakes were overlaid across the gap between the two end electrodes (figure 5(a)) followed by tip-induced drawing of the rGO channel between the electrodes and extending typically $\sim 3 \mu m$ onto each of the end electrodes (figure 5(b)). Thus, the observed non-linearity of the lateral I–V characteristics will bear contributions from transport along the rGO channel and that across the rGO-electrode interfaces. Since the tip-induced modification happens primarily on the top surface of GO, the underlying electrode interface, buried below the GO flake will likely be impacted to a lesser extent. The systematic decrease in non-linearity, as evidenced through the variation of the parameter $G(1 V)/G_0$ (figure 7(b)) with the number of scans (progressive reduction) allows us to deduce that the I–V characteristics are dominated by the electrical and electronic nature of the GO material rather than by charge transport across the electrode interfaces. Furthermore, the potential map biases in figure 5(c) all clearly indicate flat regions (constant potential) at the two ends that correspond to the rGO regions lying on the electrodes, which is indicative of stable and uniform electrical contact between the rGO channel and...
underlying electrodes. The residual non-linearity retained in the most reduced state of the rGO devices is likely representative of the non-linearity arising at the end contact interfaces. However, the highly inhomogeneous nature of the material makes it very difficult to quantify the nature of transport at the contacts. Experimentally, the IVs recorded after the first few tip scans, close to the noise floor of the measurement system, showed voltage offsets akin to charging between the source–drain electrodes of the order of few 10 s of mV. The offsets systematically decreased after the increased number of scans, becoming non-existent after the 30th scan.

The above results suggest a disordered conductor with a depleted DOS at its $E_F$, which progressively fills up with the increased number of scans. That is, for pristine GO, its $E_F$ lies within its band gap ($E_G$) with zero DOS at $E_F$, and with progressive reduction scans results in the addition of localized states around its $E_F$, increasing its graphene-like character. For GO, the typical energy required for the carriers to become delocalized and conduct (i.e. the activation energy) is determined by $E_G$, but the band diagram becomes complicated for the inhomogeneous rGO. For rGO, carriers need to overcome a localization energy quantified by the parameter $V_0$ in equation (1). Figure 7(d) plots the decrease in the best fit values of $V_0$ with the increased number of scans, indicating that the localization energy the carriers have to overcome decreases progressively. As mentioned earlier, previous investigations on the temperature dependence of conductivity identify electrical transport in rGO to be driven by Mott-VRH, ES-VRH and activated transport. However, the domain of validity of such identification and more importantly the consequences of such identification remain unclear. Our results show that devices with lower final values of rGO channel conductance (more insulating, $R \sim 300 \, \text{k}\Omega$) show thermally activated transport, while those with higher final conductance (less insulating, $R \sim 50 \, \text{k}\Omega$) follow the Mott-VRH model for 2D systems for the temperature range investigated. Supplementary figure 4 evidences the linear dependence of $\ln G$ on $1/T$, for the low-conducting devices (D1 and D2), indicating Arrhenius-type fits yielding activation energies $E_a$ with values 166 and 138 meV, respectively. In contrast, the more conducting devices (D3 and D4) show a

Figure 7. Non-linear charge transport and its evolution with progressive reduction of rGO. (a) Lateral IV characteristics of a two-terminal rGO device at different states of tip-induced reduction. (b) Zero-bias conductance as a function of the number of scans presented on the left axis; the right axis shows the device non-linearity represented by $G(1 \, \text{V})/G_0$ as a function of the number of scans. (c) $\ln(G/G_0 - 1)$ versus $\ln(V)$ plot at different reduction state of the rGO device. Parameter $V_0$ was calculated from the linear fit in the low-bias regime of plot c. (See in the writing section) (d) Variation of $V_0$ with the number of scans performed for the reduction of GO.
linear dependence of \( \ln G \) on \( 1/T^2 \) (see supplementary material for further details). The limited temperature range explored for the more insulating samples resulted from the limitations in the maximum measurable resistance in the experimental setup.

As mentioned earlier, electrical transport in rGO systems has been variously shown to follow thermally activated transport or 2D-VRH, both Mott-VRH or field controlled ES-VRH. An advantage of the present tip-induced reduction technique is the ability to conduct controlled reduction and thus investigate electrical transport in rGO at intermediate states of reduction. The highly disrupted \( sp^2 \) network of GO and presence of oxidative functional groups is reflected as a bandgap opening at the Fermi level of graphene. Although progressive reduction locally restores the \( sp^2 \) network and conducting domains, it does not form a percolative path before a critical fraction is nucleated. Within the band picture, this is reflected as an effective reduction in the band gap of this highly inhomogeneous system, allowing carrier transport by thermal excitation, which is evidenced in the earlier stages of reduction and in the more resistive samples (figure S4(a)). For samples with higher degree of reduction and increasing number of \( sp^2 \) domains, the system nears the percolation threshold with higher incidence of localized states close to the Fermi level \( (E_F) \). Transport in this regime would be mediated by carriers hopping across localized states near the \( E_F \), lying within the band gap of the pristine GO. The density of such localized states, their energies \( (\epsilon_r) \) and occupation being determined by the degree of reduction of GO, i.e. the number of scans. Electrons in these localized states have a hopping probability determined by the spread in \( \Delta \epsilon_r \) vis-à-vis spatial separation between the states (domain size \( \sim r \)) [25], which are all dynamically controlled by the degree of reduction. In the relatively lower-resistance devices (more reduced), the plots in figure S4(b) show that 2D-VRH is the dominant transport mechanism in this regime. However, the large local field variation evidenced in the surface potential maps also indicates that ES-VRH would likely play a significant role in this reduced regime, as has been reported previously in epitaxially grown graphene [27]. Last, the \( IV \) analysis yields an effective localization potential in \( V_0 \), which is the cumulative response across the highly inhomogeneous rGO system, harbouring the graphitic domains in the GO background. Our present results do not allow us to draw more detailed inferences but to conclude that transport along the rGO system would demonstrate activated transport towards the initial stages of reduction, which changes over to VRH transport under progressive reduction with significant cross-over between the various stages of reduction. The exact nature being decided by the band gap, nucleation and the energetics of the localized states close to the \( E_F \) and temperature.

**Conclusion**

In conclusion, we have investigated the fabrication of reduced GO devices, individually written onto insulating GO flakes by nanoscale local reduction using a C-AFM tip. The reduction process offers a high degree of control and standardization through three macroscopic parameters, junction bias, RH and number of reduction cycles, controlling the degree of reduction. Change to the morphological and electronic properties of the GO surface after reduction, investigated using spatially resolved electrical measurements and micro-Raman spectral mapping, provided conclusive evidence towards the reduction of GO in the designated area. Electrical transport through the two-terminal rGO channels is non-linear, which correlates well with the spatially resolved 2D surface potential maps. The variation reflects the inhomogeneous electronic structure across the surface and segregation into local positively and negatively charged regions. The \( I-V \) characteristics showed systematic decrease in non-linearity with progressive reduction of the channel, indicating that the non-linearity originates from the material properties of rGO, rather than transport across the terminal metal-rGO contacts. Together, temperature and bias-dependent transport, and the conductance and potential maps give further evidence of charge localization effects close to the Fermi level with multiple transport mechanisms contributing to the overall conduction. Depending on the degree of reduction and the disorder in the system, electrical transport in rGO may be dominated by thermally activated or Mott-VRH, or carry signatures of electric-field-driven variable range hopping, due to the high local fields that are significantly stronger than the applied average field. The findings not only provide for better understanding of the nanoscale electronic structure of rGO and electrical transport, but demonstrate the scope of tuning its electronic and electrical properties by restoration of the \( sp^2 \) hybridized carbon lattice. It is anticipated that these results will further the scope towards the realization of all graphene electronic devices such as transistors, switches and tuneable infra-red detectors, leveraging not only the technical control allowed by this scheme, but the functional aspects of the investigation.

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**Data availability statement**

All data that support the findings of this study are included within the article (and any supplementary files).
Author contributions

J M, S R P S and K B conceived the project. Arijit, H G, K B, A K and J M performed the experiments. Arijit and J M analyzed and interpreted the data. All authors contributed to writing the manuscript.

Competing interests

The authors declare no competing financial interests.

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