Electron–phonon interaction in bulk layered graphene and its oxide in the presence of alcohols in a device: equilibrium molecular doping†

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We report on electron phonon interactions in bulk layered graphene (GRA) and its oxide (GO) under bias when exposed to 1° or 2° alcohol vapors, where we have focused on the change of Raman intensity of G and D bands as a function of the bias across the device. In addition to the softening of phonons we have observed a systematic variation in the intensity for D and G bands which is directly related to guest molecules and intrinsic surface nature of GRA and GO. Although the guest molecules withdraw electrons from GRA or GO, the intrinsic nature of the host material has caused mutually contrasting behaviour in IV-characteristics, where the conductance of the former decreases while it increases for the latter. The results from IV-spectra and the intensity maps of D and G bands are juxtaposed and the changes are analyzed with respect to surface and functional group interactions. In the context of doping, it is interesting to see that under equilibrium molecular charge transfer (top-gate like), the intensity ratios of 2D and G bands are not constant in contrast to a previous study [Phys. Rev. B., 2009, 80, 165413] in which such a ratio is invariant in the field effect configuration.

Introduction

Graphene based sensors are of recent research interest among which detection of single molecules is noteworthy. In any case the sensor works on the basis of a change in conductivity of a host in the presence of a guest (test gas). The change in conductivity is a result of charge transfer, where two mechanisms are generally possible. They are (i) the relative positions of HOMO/LUMO of a host with respect to the Fermi level (E_F) of the host favoring transfer of electrons; or (ii) the mixing of the HOMO/LUMO of a guest with those of the host producing hybrid orbitals. In other words, the E_F of graphene is proportional to the square root of the carrier concentration which is shifted when doped because of stiffening or softening of phonons. Note that the phonon dispersion is modified when the carrier concentration and mobility are altered. Despite the fundamental importance of host–guest chemistry, the sensitivity of the device is commonly studied for improvements. The ratio between the intensities of 2D and G peaks from bulk layered graphene (GRA) is almost invariant for various doping densities in a field-effect-configuration, however, in the context of molecular charge transfer, we believe that the relative intensity changes of D and G bands of GRA and its oxide (GO) are inevitable to unveil the host–guest chemistry. Albeit molecular charge transfer is known when the surface is treated with test molecules however, the electron–phonon interaction is not well-studied in the presence of guest molecules. In this direction in situ Raman spectroscopy is employed to detect the electron–phonon interaction in the presence of guest molecules in a device structure.

Ethanol (EtOH) and isopropanol (IPA) were chosen as model molecules (guests) based on the fact that the activity of the –OH group depends on the electron directing or withdrawing nature of the functional group that it is attached to and the structural differences when a molecule orients on the surface. Furthermore, the absorption energies against the position and orientation are also important factors to consider. See H2O (acceptor) clusters on graphene for geometric structure and energetics in conjunction with gas phase conformers for EtOH (e.g. trans and gauche) and IPA. In situ Raman spectroscopy is performed in the presence of model molecules when GRA and GO are biased in a device structure. We have noticed an anomalous and mutually contrasting behavior of the intensities of G and D bands as well as the conductance of the GRA and GO devices which purely originates from the bias dependence of molecular desorption. Notably, the intercalation of test
vapors is not evidenced in the present case from X-ray diffraction studies. As expected EtOH and IPA differ from each other in the electron withdrawing nature and clearly show their influence on the intensity of G and D bands from GRA and GO. The results from EtOH and IPA are compared with that of the ambient atmosphere (Atm) for a detailed understanding. It is also inferred that the intensity ratio, $A(2D)/A(G)$, is not constant for any of the three cases. This study not only addresses the host–guest chemistry (or top-gate equilibrium molecular charge transfer) in the potential materials such as GRA and GO, but also suggests a very good platform for computational studies in the context of the absorption energy, position and orientation in conjunction with the intensity of G and D bands in a resistive type sensor under bias. In order to design future generation sensors with the capability of detecting single and selected molecules a better understanding of the host–guest chemistry is vital, especially in the case of bio-sensor applications where target specific sensing is of utmost importance. Starting with smaller molecules such as EtOH and IPA in the gas phase may be a wise option to understand such weak interactions using Raman spectroscopy in the background of complex functional groups present on GO and the inevitable edge of GRA.

Experimental

Scanning electron microscopy (SEM) was performed with a FEI Quanta 200 FEG. Transmission electron microscopy (TEM) was performed with a FEI-Tecnai G2 F30 while the samples were dispersed in de-ionized water and a tiny droplet was analyzed from a holey carbon coated TEM grid. X-ray diffraction patterns (XRD) were obtained from a PANalytical X’pert Pro MPD ($\lambda = 1.5418$ Å). The ionic state of carbon at the surface of the samples was investigated by X-ray photoelectron spectroscopy (XPS, ThermoScientific K-Alpha, Al Kz-$\hbar$ = 1486.6 eV) with a flood-gun charge neutralizer. Raman spectroscopy was performed with WITec instruments (Alpha 300S, 532 nm laser). Raman-intensities here are the areas under the corresponding fraction pattern, and (d) corrugated edges from GO.

Results and discussion

The SEM images from GRA suggests a typical flake-like structure in contrast to GO which has shown an exfoliated nature similar to a previous observation [Fig. S2 of ESI†]. The sponge like structure is typical to exfoliated graphene. The modified morphology is the primary confirmation of exfoliation, where we can see the influence of the acid treatment as expected.

TEM images are recorded on GRA and GO samples and representative images are shown in Fig. 1. From the low resolution images of GRA (Fig. 1a) we can see the flake like structure consistent with the SEM observation. In Fig. 1b GRA has shown very clear overlap of graphene sheets which are nearly straight lines. The distance between the sheets is found to be $3.4 \pm 0.06$ Å (estimated by measuring 5 planes). A SAED pattern (Fig. 1c) is recorded on GRA which has shown well defined circles with bright spots, implying predominant crystalline phases. The crystal planes are annotated on the image. It is notable that the layers are perfectly parallel; however, their mutual orientation within the plane is random (turbostatic) which is seen as circles in the SAED pattern. The first diffraction ring (002) is slightly diffused revealing that it harbors crystal planes of slightly varying distances. In Fig. 1d we have shown a HRTEM image from GO, and the stacked planes can be seen which are of...
course not straight lines like the case with GRA (Fig. 1b). This morphology is expected, as the edges are functionalized with various chemical groups including the basal plane. The wrinkled morphology is similar to previous reports where the authors have used the Brodie process or modified Hummers method to prepare GO. It is also suggested that there may be some un-reacted GRA within the sample, which may be feasible even in the present case.

XRD patterns from GRA and GO samples are shown in Fig. 2a and b, while XPS from GO is shown in Fig. 2c. Both the samples have shown sharp diffraction peaks indicating the crystalline nature of the samples. The angular location of the peak matches with the literature and the corresponding reflections are annotated on the image. We would like to draw attention to the peak corresponding to the (002) reflection (c-axis, normal to the hexagonal planes) in both the samples. After oxidation, the (002) peak has shown a shift to lower 2θ values. Moreover, the second order reflection (004) can also be seen for both the samples. It is also interesting to see that the relative intensities of (002) to (004) for the GRA case are as high as 33 in contrast to 10 from GO. This suggests that GO sheets are more random and have been exfoliated successfully. Furthermore, the calculated interplanar spacing of GRA and GO is ~3.368 Å and ~9.135 Å, respectively. The lattice spacing for the case of the GRA sample is consistent with the measurements from TEM. The d value after oxidation depends on the procedure and level of oxidation, while an increase from GRA is a clear consequence of functional group implantation on the basal planes as well as edges of individual graphene sheets. On the other hand, this increase causes a loss in the 3D crystallinity. In contrast to a single (020) reflection from GO, for the case of GRA the 40–48° region contains multiple peaks (inset of Fig. 2b).

Interestingly, after oxidation these multiple peaks were not present within the detection limits. To reiterate the aim of this report, we would like to understand the intensity changes in D and G Raman bands in the presence of alcohol vapors while ruling out the formation of intercalated compound is necessary. In the context of intercalation with alcohols, d has been altered significantly. Hence diffraction analysis is performed on the samples and as an example, the pattern from GRA under EtOH vapor exposure is shown in Fig. S3 of ESI.† The result suggested a null effect on d.

The electronic and optical properties of GO and reduced GO depend on the concentration of major functional groups such as epoxides, hydroxyls and carbonyls. For this, we have analyzed a C 1s core-level spectrum to determine the various functional groups as a consequence of oxidation. Broadly, the spectrum has shown two major and one minor peak before deconvolution (Fig. 2c). The result of the peak deconvolution suggests that the composite peak structure constitute four functional groups viz. C=C, C–O, C=O and O=C=O. The energetic location of C 1s in each functional group is annotated on the image, which is found to be in line with the literature. The area ratios are 0.99, 0.56, 1 and 0.13 for C=C, C–O, C=O and O=C=O, respectively. As a whole on the surface the sp² C=C : oxidized-C ratio of the GO sample is ~1.7 : 1. During the oxidation process, charge transfer takes place from GRA to oxygen in all the above functional groups, while the electron density is majorly on the oxygen atom(s) because of its relatively high electronegativity.

The schematic of Raman processes that GRA can host is shown in Fig. 3a (ref. 9) by following the nomenclature suggested by Ferrari et al. Raman spectra from GRA and GO devices are shown in Fig. 3b and c for the zero bias condition. The spectral location of each band is annotated in Fig. 3a and b, which are consistent with the literature. Contextually, it would be appropriate to discuss the origin of various bands where we refer Fig. 3a for all five processes. (i) G-band: originates from sp² hybridized C=C bonds and unambiguously assigned to zone centre LO phonon modes of symmetry. The spectral location of this band is independent of the excitation energy in the case of GRA. (ii) D-band: attributed to ‘unorganized’ carbon and small sized graphite crystals or boundaries of larger crystals, which are essentially the breathing modes of sp² atoms in rings. Notably the origin of the D-band is attributed variously where either the selection rules are replaced or a double resonance (DR) phenomenon is introduced. According to Ferrari the DR mechanism is more suitable, which also explains the excitation dependent spectral location of the D-peak (due to the Kohn anomaly at $K$). (iii) 2D-band: an inter valley process and formerly known as $G^{\prime}$ however, it is D overtone. (iv) D’-band: an intravalley DR process, which connects two points belonging to the same cone around K (or K’). (v) 2D’-band: this band corresponds to the second order intra-valley D’ peak.

As mentioned in the introduction of this report, the present context deals with the intensity levels of G and D bands. To emphasize the G peak is a one phonon ($E_{2g}$) process at the Brillouin-zone center. i.e. the electron is excited to the unfilled
The linear relationship 

\[ I_\text{1570} = \frac{C_{24}}{240} \]

is taken into account while considering the case with graphene where the G band up-shifts upon hole and electron doping.\(^7,10\) it would be premature to suggest a shift in the case of GRA or GO.\(^7,13,15,16\) We will address this while discussing the electrical measurement more clearly. Notably, the spectral location of \( C_{\text{GRA}}^{G} \) \( C_{\text{GRA}}^{D} \) and \( D_{\text{GRA}}^{G} \) cases represents a combined effect from the electron donating or withdrawing gaseous molecules in the atmosphere while \( \delta_G \) or \( \delta_D \) is an ensemble effect from a laser spot of \( \sim 300 \) nm diameter.

As outlined in the introduction two charge transfer mechanisms are feasible, however the dangling orbitals are more prone to hybridization which is dependent, of course on the extent of orbital overlap.\(^3\) Furthermore, the difference in the electronegativity of the atoms in the proximity of the surface govern the polarity and the magnitude of the bond dipole in the background of an inductive effect from neighboring groups. The interacting orbitals of GRA are chemically different from that of GO due to its oxygen containing functional groups.\(^3\)

Note that unoxidized portions of GRA still exists in GO. Hence in the GO case surface adsorption of guest molecules would be position dependent where the functional groups and their intrinsic nature play a major role.\(^3,14\)

In a previous study\(^11\) the sensor is treated with test liquids directly, while here we have exposed it to the test vapors. In the former case the molecules are physically existing on the surface in contrast the test molecules are in equilibrium state and electronically interacting. The IV-spectra from GRA and GO devices under three different environments are shown in Fig. 4 on a semilog scale and in Fig. S4 of the ESI. The results of linear fit close to zero bias are tabulated in Fig. S5 of the ESI.\(^1\) From Fig. 4, for a similar bias condition the current carried by GRA is nearly three orders higher than its oxide counterpart for similar device dimensions. The reason for increased resistance is nothing but oxidation, where it disrupts the \( sp^2 \) conjugation and the conduction takes place via isolated \( sp^2 \) clusters. If we keep aside the quantitative differences, it is also inferred that under exposure to EtOH or IPA vapors the resistance of the GRA-device increases in contrast to that of GO-device which has shown decreased resistance. The quantitative response \( \Delta R_{\text{Host}}^{G} \) from each device and the band diagram are shown in Fig. 5a and b, respectively. The increase in resistance is denoted by the + sign while decrease is denoted by the –ve sample. In the case of GO, the comparable intensity of G and D bands is due to the increased \( sp^3 \) character, see the discussion of XPS results.\(^12,13,14\) Notably there is no detectable signature of amorphous carbon from GRA and GO (spectral range not shown here). The bands, \( G_{\text{GRA}}^{G} \) and \( D_{\text{GRA}}^{G} \) have shown a significant red-shift upon exposure to EtOH or IPA vapors. This effect is similar for \( C_{\text{Atm}}^{G} \) and \( D_{\text{Atm}}^{G} \) cases. Furthermore, \( C_{\text{Atm}}^{G} \) is red-shifted from \( G_{\text{GRA}}^{G} \) which can be understood based on the fact that the oxidation removes the electrons from the GRA.\(^33,35,36\) Furthermore at an appropriate oxidation level the process may yield a p-type semiconductor.\(^31,36\) This oxidation process is permanent where the oxygen functional groups are covalently attached; in contrast, the presence of EtOH or IPA is temporary via shift of charge carriers. The shift of these bands is because of the change in the carrier concentration and consequently shift of \( E_p \).\(^3\) While considering the case with graphene where the G band up-shifts upon hole and electron doping,\(^7,10\) it would be premature to suggest a shift in the case of GRA or GO.\(^31,35,36\) We will address this while discussing the electrical measurement more clearly. Notably, the spectral location of \( C_{\text{Atm}}^{G} \) \( C_{\text{Atm}}^{D} \) \( D_{\text{Atm}}^{G} \) and \( D_{\text{Atm}}^{D} \) cases represents a combined effect from the electron donating or withdrawing gaseous molecules in the atmosphere while \( \delta_G \) or \( \delta_D \) is an ensemble effect from a laser spot of \( \sim 300 \) nm diameter.

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In a previous study\(^11\) the sensor is treated with test liquids directly, while here we have exposed it to the test vapors. In the former case the molecules are physically existing on the surface in contrast the test molecules are in equilibrium state and electronically interacting. In contrast to previous studies\(^28,30\) where clear shoulders corresponding to \( 2D_1 \) and \( 2D_2 \) components are seen. In the case of GO the \( 2D \) peak is not seen explicitly apart from a small feature. The crystallite size is calculated to be \( 106 \) Å when the intensity ratio in the Raman signal \( (I_{1355}/I_{1570} = 0.44) \) is taken into account (value estimated from the graph).\(^4\) However, this method underestimates the crystallite size due to the dominant effect from small crystallites.\(^13\) The linear relationship\(^12\) suggests that the Raman intensity is proportional to the ‘boundary’ in the state and recombines with the hole. Whereas the \( D \) peak is an intervalley process due to the breathing modes of six-atom rings activated by a defect, i.e. excitation of an \( e^-h^+ \) pair, electron–phonon scattering with an exchanged momentum, and scattering at a defect and finally \( e^-h^+ \) recombination.\(^9\) In this report we will refer each Raman-band as ‘Band_{Guest}’ and its intensity as \( A_{\text{Band}_{\text{Host}}} \) for simplicity. For example, the G band from GRA in the presence of EtOH vapor is referred to as \( C_{\text{GRA}}^{G} \) and its intensity as \( A_{\text{GRA}}^{G} \). Shifts of each band are annotated with \( \delta \) where the suffix corresponds to a certain band. The \( 2D \) band from GRA is found to be almost symmetric (Fig. 3b) in contrast to previous studies\(^28,30\) where clear shoulders corresponding to \( 2D_1 \) and \( 2D_2 \) components are seen. In the case of GO the \( 2D \) peak is not seen explicitly apart from a small feature. The crystallite size is calculated to be \( 106 \) Å when the intensity ratio in the Raman signal \( (I_{1355}/I_{1570} = 0.44) \) is taken into account (value estimated from the graph).\(^4\) However, this method underestimates the crystallite size due to the dominant effect from small crystallites.\(^13\) The linear relationship\(^12\) suggests that the Raman intensity is proportional to the ‘boundary’ in the state and recombines with the hole. Whereas the \( D \) peak is an intervalley process due to the breathing modes of six-atom rings activated by a defect, i.e. excitation of an \( e^-h^+ \) pair, electron–phonon scattering with an exchanged momentum, and scattering at a defect and finally \( e^-h^+ \) recombination.\(^9\) In this report we will refer each Raman-band as ‘Band_{Guest}’ and its intensity as \( A_{\text{Band}_{\text{Host}}} \) for simplicity. For example, the G band from GRA in the presence of EtOH vapor is referred to as \( C_{\text{GRA}}^{G} \) and its intensity as \( A_{\text{GRA}}^{G} \). Shifts of each band are annotated with \( \delta \) where the suffix corresponds to a certain band. The \( 2D \) band from GRA is found to be almost symmetric (Fig. 3b) in contrast to previous studies\(^28,30\) where clear shoulders corresponding to \( 2D_1 \) and \( 2D_2 \) components are seen. In the case of GO the \( 2D \) peak is not seen explicitly apart from a small feature. The crystallite size is calculated to be \( 106 \) Å when the intensity ratio in the Raman signal \( (I_{1355}/I_{1570} = 0.44) \) is taken into account (value estimated from the graph).\(^4\) However, this method underestimates the crystallite size due to the dominant effect from small crystallites.\(^13\) The linear relationship\(^12\) suggests that the Raman intensity is proportional to the ‘boundary’ in the
The phenomenon that takes place causing contrasting behavior of GRA and GO is rather complex and discussed in the following although Raman spectra indicate a transfer of charge among the guest and the host. Furthermore, in contrast to ref. 11, GRA and GO-devices have shown a nonlinear response (Fig. S4 of ESI†) for higher bias conditions which suggests the variation in the conduction mechanism and warrants further investigation. On the other hand, the surface adsorption of the guest molecules might not be uniform throughout the surface of GO due to the band bending and associated charge accumulation, see Fig. 5b.

In plane and out of plane conductivities are cumulatively reflected in a GRA-device where there exists a π–π interaction \( (d = \sim 3.368 \text{ Å}) \) between the sheets (Fig. 5c). This is in contrast to the GO-device, where the charge carrier delocalization is limited to the surface via sp\(^2\) domains, however, may be not across the sheets \( (d = \sim 9.135 \text{ Å}) \) as prominent as in the case of GRA. Upon exposure to guest molecules, \( \Delta R_{\text{Guest}} \) from these devices is mutually contrasting, viz. \(+ve\) and \(-ve\) \( \Delta R \) for GRA and GO cases, respectively. The \(+ve\) \( \Delta R_{\text{GRA}} \) is because of decreased carrier–carrier scattering when some of the electrons are captured \( (e_{\text{CPR}}) \) by guest molecules (Fig. 5c). If \( e_{\text{CPR}} \) takes place \( via \) a relatively stronger bond then as expected \( \Delta R_{\text{GRA}} > \Delta R_{\text{IPA}} \) in the light of differences in the acidic nature of guest molecules, \( e_{\text{CPR}} \) takes place in the case of GO also, however, additionally guest molecules can form a dipole-type bond with epoxy groups (Fig. 5c). However, geometric orientation and kinetics therein play a major role in the \( e_{\text{CPR}} \) interaction with functional groups.3,5,14 Furthermore \( \Delta R_{\text{GRA}} < \Delta R_{\text{IPA}} \) is because of the intrinsic nature of the host materials and elaborated in the following. To transform an electron rich material into a p-type material, in principle the free electrons should be withdrawn in addition to those paired with holes. For the GO-device the level of oxidation determines the nature of conduction.33 If all of the electrons are not withdrawn by the functional groups then the majority carriers are still electrons although not as dense as parent GRA. Such low density of electrons when subjected to the \( e_{\text{CPR}} \) process results in a significant conductance changes. Note the other possibility of transfer of electrons from the guest to the relatively more acidic functional groups (other than epoxy) lead to an increase in the density of electrons in GO thereby increasing the conductance (i.e. \(+ve\) \( \Delta R_{\text{GO}} \)). Since \( \Delta R_{\text{Guest}} \) is not \(+ve\) the only possibility is \( e_{\text{CPR}} \) by guest molecules and hence the observation of \( \Delta R_{\text{GRA}} > \Delta R_{\text{IPA}} \) is satisfied. On the other hand if the GO is a complete p-type material, then the majority carriers are holes in which case the interaction of the guest with epoxy functional groups is predominant. This interaction causes a shift of charge from GO to guests increasing the conductance. Moreover, other functional groups which are more acidic than EtOH can withdraw electrons from guests there by partially neutralizing or at least trapping the holes which decreases the conductance \( (\sim ve\) \( \Delta R_{\text{GO}} \)). Having said that it may not be possible to rule out any of the above interactions between functional groups and guest molecules, where an integral effect is reflected in the IV-spectra.

Raman spectra under selected bias conditions are shown in Fig. 5b of ESI† for GRA and GO cases in three different environments. As mentioned previously, Basko suggested that \( A(2D)/A(G) \) is almost invariant for GRA in the field effect configuration.41 In this direction, we have performed a similar analysis and the results are shown in Fig. S7 of ESI†. It would be appropriate to discuss the reasons for the variation and changes in the trends for three cases as it requires foreknowledge of behavior of G and D bands in the presence of test vapors. Moving to the main motto of this report, we believe that it would be rather useful to consider the defect scattering in GRA and GO especially in the context of molecular charge transfer in a
simple resistive type sensor. The results of the host–guest chemistry on $A(G^{\text{Guest}})$ and $A(D^{\text{Guest}})$ are shown in Fig. S8 of the ESI† under both bias conditions. The symmetric response is expected as the device has symmetric structure (Fig. S1 of the ESI†). For a better representation only one polarity is shown in Fig. 6.Crudely, under relatively higher bias conditions (>9 V) all cases have shown a kind of saturation towards low and high intensities for GRA and GO cases respectively, c.f. $+ve \Delta R^{\text{GRA}}_{\text{Guest}}$ and $-ve \Delta R^{\text{GO}}_{\text{Guest}}$. However, the features appeared like a process with two transitions. $A(G^{\text{Atm}})$ is almost constant until $\sim0.01$ V and then fall rapidly with increasing bias. After this sudden fall, $A(G^{\text{IPA}})$ and $A(G^{\text{EtOH}})$ have retraced each other and appeared like they are saturating (Fig. 6a) at relatively higher bias. Notably $A(D^{\text{EtOH}})$ stayed within 0.6 to 1 on the normalized scale for all bias conditions, while the transition has taken place slightly $<0.1$ V after which it has decreased. Quite distinctively, two transitions can be seen for $A(G^{\text{IPA}})$ yielding intensity levels which are initially constant, then suddenly rise and are constant, in the said sequence (Fig. 6b). Moving onto the defect activated D band, $A(D^{\text{GRA}}_{\text{Atm}})$ has shown two clear transitions and however not retracing the $A(D^{\text{GRA}}_{\text{IPA}})$ as its G counterpart did. On the other hand the $A(D^{\text{EtOH}})$ case is similar to its G band counterpart. The behavior from $A(D^{\text{Atm}})$ and $A(D^{\text{EtOH}})$ is comparable with an exception of the transition, where they appear to saturate from $\sim0.006$ V and $\sim0.04$ V respectively. $A(D^{\text{IPA}})$ has almost shown two transitions similar to $A(G^{\text{Atm}})$ and $A(G^{\text{IPA}})$. The reasons for this peculiar though interesting behavior are explained in the following.

In a broader context, the changes in the carrier concentration and mobility alters the phonon dispersions and its intensity. $^3$–$^8$ Largely similar behavior of $A(G^{\text{Atm}})$ and $A(G^{\text{IPA}})$ can be due to the weak interaction between the host and the guest similar to the gases in the atmosphere. While, the behavioral difference between $A(G^{\text{IPA}})$ and $A(G^{\text{EtOH}})$ can be due to the variance in the $e^{-cptr}$ efficiency. These are notably, related to geometry of the molecule and the location on the surface.$^3$–$^5$ The overall trend of intensity changes with increasing bias can be understood in conjunction with the host–guest interactions and nonlinear IV-responses. The nonlinear IV suggests the varying resistance of the device with voltage. As the voltage increases the higher electric field perhaps pull the electrons back into the system. This is applicable to both GRA and GO devices. In the case of GRA, the increase of charge carrier density increases the scattering and decreases the intensity of G or D bands. For the GO case, since the electron density in GO is quite low, relatively higher bias conditions increases the electron density and hence the intensity of the G or D band.

The multistep process can be because of the differences in the binding of energy of captured electron which were released back into the system under different bias conditions. In connection to the interaction with functional groups (GO case) it would be rather difficult to unambiguously determine the breakage of these interacting bonds. Previously we have discussed that EtOH can strongly bind to the surface in the $e^{-cptr}$ process (|η| > |ζ|). Stronger binding may not necessarily reflect a complete transfer of electrons. The case with EtOH is quite interesting in both GRA and GO cases as it has shown one transition for all four contexts. This suggests that the EtOH molecules form two types of bonds with the surface. If we see the results from GO it appears to be the case that Atm and EtOH are similarly working in clear contrast to the IPA case, where the second transition for $A(G^{\text{IPA}})$ is at $\sim1$ V. Hence IPA perhaps binds to the surface by $e^{-cptr}$ with two binding energies. As mentioned previously, in the following we discuss the reasons for the variation in the trends of $A(2D)/A(G)$.

In the field-effect-configuration, the $E_F$ is manipulated via changing the gate voltage, which can be controlled externally. Given that the present device structure is similar to the top gate configuration, the gate voltage is analogous to the transfer of charge by the guest molecules. Interestingly, $A(2D)/A(G)$ is not constant either for GRA or GO cases. This suggests that the gate voltage applied by the molecular charge transfer may not be constant for all bias conditions. When the guest molecules are interacting with the defects the intensity changes in the 2D band are expected. Hence the different trends in the $A(2D)/A(G)$ for three cases are because of the variations within the molecules and the way they interact with the surface. As explained previously, when it comes to equilibrium molecular doping, as in the present case, the molecules are bound to the surface within the lines of thermodynamic equilibrium, where their

![Fig. 6 Raman intensities for three environments under selected biases. The G band from (a) GRA, (b) GO; the D band from (c) GRA and (d) GO. The spectra are normalized against the intensity at zero bias. 0 V is manually assigned on the log scale.](image-url)
binding energies against applied bias needs to be taken into consideration. This is the core of various reasons for different trends seen in Fig. S7 of ESL† To emphasize, the surface binding depends on the ‘molecule’ its orientation and physical location (in case if it prefers a ‘defect’). Previously discussed points such as $|\eta| > |\zeta|$ and voltage dependent molecular desorption etc. should also be taken into account. Given the above complexity of the variations those that were observed from Fig. S7 of the ESL† demand further investigation.

Conclusions

In this report, we have studied electron phonon interactions from GRA and GO in a simple resistive type sensor. These sensors were exposed to saturated EtOH or IPA vapors under biased conditions. We have focused on the change of the Raman intensity of the G and D bands as a function of the bias across the device in the presence of test vapors. Upon exposure to either EtOH or IPA softening of phonons is observed, where the guest molecules withdraw electrons from both devices. Moreover, we have noticed mutually contrasting changes in resistance for GRA and GO devices. These devices have shown a nonlinear $I$/$V$-response in contrast to the existing literature. For the case of the GRA-device the resistance is increased due to a decline in the carrier–carrier scattering, with the effect of the guest molecules capturing free electrons. The situation is completely different for the GO device, where the resistance of the device is decreased because of complex interactions such as dipole-type bonds apart from the $e^–_\text{epm}$ process similar to GRA. The consequence of these interactions and possibility of involvement of other functional groups are addressed. Furthermore the quantitative response from GRA is lower than GO, where the intrinsic nature of the host materials play a crucial role. We believe the intensity changes of D and G bands is not invariant for GRA in the present equilibrium top gate-like configuration. Broadly, the intensities behaved in contrast to each other and can be treated similar to the change in the resistance under exposure to guest molecules. We note that these intensity changes are not because of the solvent intercalation. $A(2D)_\text{GRA}$ and $A(D)_\text{GRA}$ were initially constant with bias and then fell rapidly under higher bias conditions and depicted a kind of saturation. Note that EtOH and IPA were exceptions in this context, which have shown one transition, i.e. only two features. $A(D)_\text{Guest}$ and $A(G)_\text{Guest}$ increased with increasing bias and showed a saturation at relatively high bias. $A(D)_\text{GO}$ has shown clear features of two transitions, i.e. initially constant then rapidly increases to finally saturate. This is not seen for either EtOH or Atm cases explicitly. The results suggest that the onset of each step depends on the guest species and their nature of bonding on the surface. Essentially the binding energy against applied bias is crucial in determining the transition.

In the case of GO the surface adsorption of the guest molecules needs to be considered carefully, as they might not adsorb uniformly due to the band bending (under bias) and associated charge accumulation. Furthermore, the interaction of guest molecules with functional groups other than ‘epoxy’ is another factor that requires reasonable attention. This needs to be juxtaposed with the geometric orientation of the guest molecules. Due to the interaction of epoxy and guest molecules the HOMO level may face a shift due to the modified electron occupancy; however, it can be inferred from sophisticated simulation studies. See for example, $H_2O$, $NH_3$, CO, NO and $NO_2$ on graphene that were studied for their absorption energies against adsorption position and orientation.†

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Notes and references


