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Effects of charge transfer interaction of graphene with electron donor and acceptor molecules examined using Raman spectroscopy and cognate techniques

Rakesh Voggu¹, Barun Das^{1,2}, Chandra Sekhar Rout¹ and C N R Rao^{1,2,3}

¹ Chemistry and Physics of Materials Unit and CSIR Centre of Excellence in Chemistry, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur PO, Bangalore-560064, India

² Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore-560012, India

E-mail: cnrrao@jncasr.ac.in

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Abstract

The effects of the interaction of few-layer graphene with electron donor and acceptor molecules have been investigated by employing Raman spectroscopy, and the results compared with those from electrochemical doping. The G-band softens progressively with increasing concentration of tetrathiafulvalene (TTF) which is an electron donor, while the band stiffens with increasing concentration of tetracyanoethylene (TCNE) which is an electron acceptor. Interaction with both TTF and TCNE broadens the G-band. Hole and electron doping by electrochemical means, however, stiffen and sharpen the G-band. The 2D-band position is also affected by interaction with TTF and TCNE. More importantly, the intensity of the 2D-band decreases markedly with the concentration of either. The ratio of intensities of the 2D-band and G-band decreases with an increase in TTF or TCNE concentration, and provides a means for carrier titration in the charge transfer system. Unlike the intensity of the 2D-band, that of the D-band increases on interaction with TTF or TCNE. All of these effects occur due to molecular charge transfer, also evidenced by the occurrence of charge transfer bands in the electronic absorption spectra. The electrical resistivity of graphene varies in opposite directions on interaction with TTF and TCNE, the resistivity depending on the concentration of either compound.

1. Introduction

The novel electronic structure and properties of graphene have attracted the attention of several workers [1–3]. The electronic structure of graphene is significantly modified by electrochemical doping with holes and electrons.

Electrochemical top gating is generally used in polymer transistors and carbon nanotubes. In the case of graphene, it has been possible to reach high doping levels through electrochemical top gating [4, 5]. Raman spectroscopy has proved to be an excellent tool for studying the effects of doping [4–6]. Raman spectroscopy provides the best signature for characterizing graphene, in that it is sensitive not only to

³ Author to whom any correspondence should be addressed.

the number of layers but also to dopant effects [4–6]. The Raman G-band of single-layer graphene around 1570 cm^{-1} stiffens and sharpens on electrochemical doping with holes as well as electrons. The responses of the Raman 2D-band around 2650 cm^{-1} appear to be different for holes and electrons. Furthermore, the ratio of intensities of the Raman 2D-band and G-band of single-layer graphene is sensitive to electrochemical doping. We considered it important to investigate the effects of doping graphene through molecular charge transfer by the interaction of graphene with electron donor and acceptor molecules and compare the results from electrochemical doping. In order to examine the nature and magnitude of changes brought about in the Raman spectrum and in the electronic structure, we have studied the interaction of graphene with tetrathiafulvalene (TTF) which is a powerful electron donor and tetracyanoethylene (TCNE) which is an excellent electron acceptor. We have employed Raman spectroscopy as well as electronic spectroscopy, the former enabling us to monitor the changes with the concentration of the donor and acceptor molecules. We have also measured the effect of interaction of the donor and acceptor molecules on the electrical resistivity of graphene.

2. Experimental details

Few-layer graphene was prepared by the exfoliation of graphite oxide by employing the literature procedure [7, 8]. Exfoliation of graphite oxide so obtained was carried out in a furnace preheated to 1050°C under argon flow for about 30 s. The graphene samples were characterized using transmission electron microscopy, atomic force microscopy (AFM) and powder x-ray diffraction (XRD). The number of layers in the graphene samples prepared by us was 4 ± 1 as indicated by AFM and analysis of the (002) reflection in the XRD pattern. Raman spectra were recorded with a LabRAM HR high resolution Raman spectrometer (Horiba-Jobin Yvon) using a He–Ne laser ($\lambda = 632.8\text{ nm}$). For Raman measurements, one milligram of the graphene sample was dispersed in 3 ml of benzene containing appropriate concentrations of TTF and TCNE and sonicated. The resulting solution was filtered through an Anodisc filter (Anodisc 47, Whatman) with a pore size of $0.1\text{ }\mu\text{m}$. Electronic absorption spectra were recorded with a Perkin-Elmer UV/VIS/NIR spectrometer. In order to study the interaction of graphene with TTF and TCNE using electronic absorption spectroscopy, the compounds were added to a suspension of graphene in acetonitrile. The suspensions were drop-coated on a quartz plate and dried. Electrical resistivity measurements were carried out by drop-coating the graphene sample on Au gap electrodes patterned on glass substrates.

3. Results and discussion

In figure 1 we show the Raman G-band of graphene recorded after interaction with varying concentrations of TTF and TCNE. We see a feature on the right side of the G-band ($\sim 1570\text{ cm}^{-1}$) due to the defect-related G' -band. With increase in the concentration of TTF, there is softening of

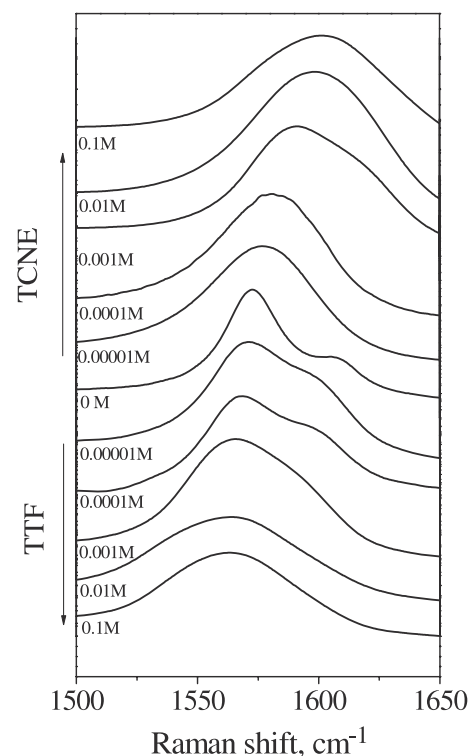


Figure 1. Shifts in the Raman G-band of graphene caused by interaction with varying concentrations of TTF and TCNE.

the G-band, while there is stiffening of the G-band with increasing concentration of TCNE. The G-band broadens with increase in the concentration of either TTF or TCNE. In figure 2(a) we show the variation in the position of the G-band maximum with the variation in concentrations of TTF and TCNE. The figure clearly shows how interaction with TTF and TCNE causes shifts in the opposite directions, the magnitude of the shift increasing with concentration. This is in contrast to the stiffening observed with electron and hole doping by electrochemical means [4, 5]. Interestingly, the full width at half-maximum (FWHM) of the G-band increases on interaction with both TTF and TCNE, as can be seen from figure 2(b). On the other hand, the G-band sharpens on electrochemical hole or electron doping. The G' -band around 1607 cm^{-1} exhibits shifts similar to the G-band ones on interaction of graphene with donor and acceptor molecules, accompanied by an increase in the FWHM.

The position of the D-band ($\sim 1320\text{ cm}^{-1}$) of few-layer graphene does not vary systematically on interaction with TTF and TCNE. The position of the 2D-band, however, does vary on interaction with TTF and TCNE, the latter causing an increase in the frequency. More interestingly, the intensity of the 2D-band decreases markedly on interaction with either TTF or TCNE as shown in figure 3(a). The ratio of intensities of the 2D-bands and G-bands, ($I(2D)/I(G)$), decreases markedly with increasing concentration of TTF and TCNE as shown in figure 3(b). This behaviour is similar to that found in the case of electrochemical doping [4]. The relative intensity of the D-band shows a behaviour different from that of the 2D-band, in that its intensity increases on interaction with donor or

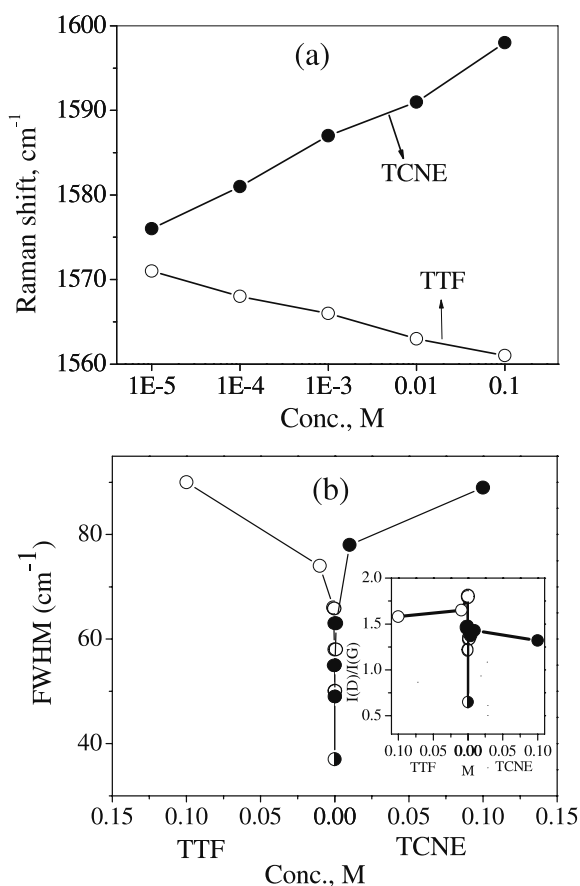


Figure 2. Variation of (a) the position and (b) the FWHM of the G-band with the concentration of TTF and TCNE. The inset of (b) shows the variation of the D/G-band intensity ratio with the concentration of TTF and TCNE.

acceptor molecules, with the minimum value in the absence of interaction. In the inset of figure 2(b), we show the variation of the $I(D)/I(G)$ intensity ratio with the concentrations of TTF and TCNE. The above results reveal how the Raman spectrum of few-layer graphene is highly sensitive to charge transfer from electron donor and acceptor molecules. Besides showing how the different Raman bands (G-bands, D-bands and 2D-bands) exhibit different sensitivities to interaction with electron donor and acceptor molecules, the present study shows significant differences between electrochemical doping and doping by molecular charge transfer. The difference between the sensitivities of the D-bands and the 2D-bands is likely to be arising because of the origins of these bands, as discussed later.

Since we consider the interaction between graphene and TTF and TCNE to be due to molecular charge transfer, we have examined the UV-visible absorption spectra of graphene with varying concentration of TTF and TCNE to look for possible evidence for charge transfer. TTF has a strong absorption band in the region of 305–316 nm, a shoulder at 361 nm and a broad band around 445 nm. The charge transfer band of TTF with aromatics is in the 400–700 nm region [9]. We find a broad band in the 500–800 nm region in the TTF-graphene system, as shown in figure 4(a). TCNE has a strong absorption band

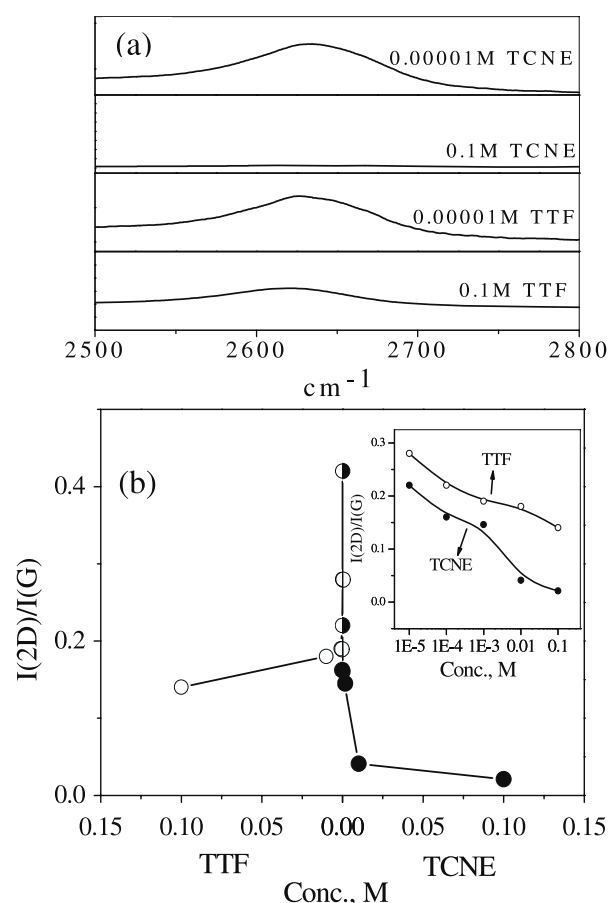


Figure 3. Variation in the (a) Raman 2D-band and the (b) 2D/G-band intensity ratio with the concentration of TTF and TCNE. The inset of (b) shows the variation of the 2D/G-band intensity ratio with the concentration of TTF and TCNE on a log scale.

in the 250–270 nm region, while the charge transfer band of TCNE with aromatics is in the 550–750 nm region [10, 11]. On interaction of TCNE with graphene, a broad charge transfer band between 520 and 800 nm is observed (figure 4(b)). In addition, bands possibly due to radical anions of TCNE seem to appear [11].

We have measured the I - V characteristics of graphene after interaction with different concentrations of TTF and TCNE (figure 5). The I - V plot always remains linear, but the slope decreases with increasing concentration of TTF and increases with increasing concentration of TCNE. Thus, the resistance increases with increasing TTF concentration, and decreases with increasing TCNE concentration. The variation of the resistance with the concentrations of TTF and TCNE is shown in the inset of figure 5(a), reflecting the dependence of the resistance on the carrier concentration.

The above results clearly demonstrate the extraordinary changes in the Raman bands of few-layer graphene brought about molecular charge transfer and also the significant differences in sensitivity of the different Raman bands to doping by charge transfer. This is a reflection of the changes in the electronic structure on electron-phonon interaction. Many of these results can be understood on the basis of following

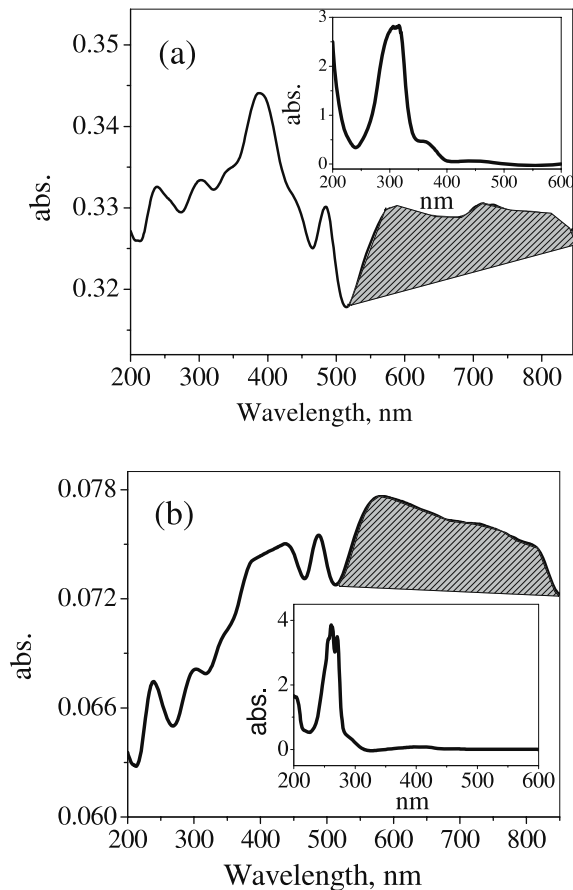


Figure 4. Electronic absorption spectra of (a) graphene + TTF and (b) graphene + TCNE. Insets in (a) and (b) show the spectra of TTF and TCNE, respectively. The shaded regions correspond to the charge transfer bands.

considerations [6]. The G-band is a doubly degenerate phonon mode (E_{2g}) at the BZ centre of the sp^2 carbon network. It is truly characteristic of the sp^2 framework. The electron–phonon coupling in graphene causes Kohn anomalies in the phonon dispersions which can give rise to phonon softening [12, 13]. Stiffening of the G-band arises from the non-adiabatic removal of the Kohn anomaly at the Γ point [14]. Broadening of the G-band suggests the absence of blockage of the decay channels of the phonons into electron–hole pairs in the present situation. The differences between the D-bands and the 2D-bands are significant, though both originate from a double-resonance Raman process. The D-band couples preferentially to the electronic states with wavevector k such that $2q = k$ [15]. It appears that an intervalley double-resonance process involving electronic states around two inequivalent K points is responsible for the D-band. Two scattering events, of which one is an elastic process involving defects and another is inelastic involving a phonon, occur in the case of the D-band. Both processes are inelastic involving phonons in the case of the 2D-band [6]. The high intensity of the 2D-band as well as the higher sensitivity of the intensity to doping may be caused by a triple-resonance process involving both electrons and holes [16].

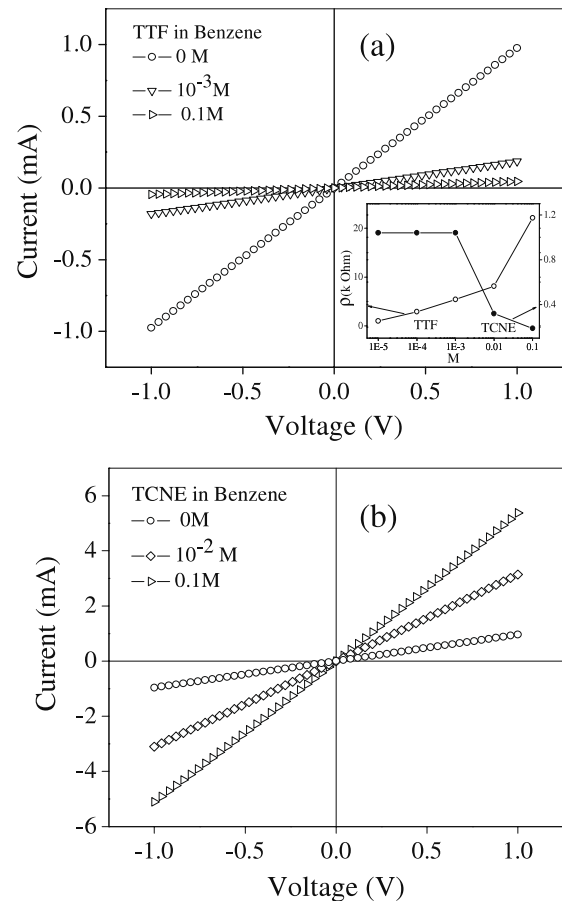


Figure 5. I – V characteristics of graphene on interaction with different concentrations (M) of (a) TTF and (b) TCNE. The inset in (a) shows the variation in the resistance, ρ , with the concentration of TTF and TCNE at a bias voltage of 0.5 V.

4. Conclusions

In conclusion, the present results establish that molecular charge transfer between graphene and electron donor or acceptor molecules causes marked changes in the electronic structure and hence in the Raman and electronic spectra of graphene as well as its electrical resistivity. The large changes in the Raman spectra observed by us may be not entirely due to charge transfer. Inhomogeneous distribution of donor/acceptor molecules, adiabatic correction as well as the nature of the graphene surface may also be contributing factors. Thus, graphene prepared from nanodiamond shows somewhat smaller charge transfer induced Raman shifts [8]. The 2D/G-band intensity ratio provides a probe for determining the magnitude of doping through charge transfer. The changes in the Raman spectra brought about by the interaction of few-layer graphene with electron donor and acceptor molecules differ to some extent from those observed on electrochemical doping of graphene [4]. It would be instructive to investigate the effects of molecular charge transfer on single-layer graphene and also carry out theoretical calculations to throw light on the effects of molecular charge transfer on the electron–phonon interaction in single-layer and few-layer graphenes. Such a study would also throw light on

the differences in sensitivity of the different bands to charge transfer and the subtle differences between electrochemical and charge transfer doping.

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