Supplementary Information

Determining Fermi level by absorption quenching of monolayer

graphene by charge transfer doping

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Transmittance of as prepared and TFSA-doped one, two and three layer graphene on quartz substrate

Each graphene layer absorbs 2.3% photon irrespective of the wavelength. As explained above the transmittance of monolayer graphene intrinsically at ~99.7% with TFSA doping saturates to 100% at all photon energy smaller than the Fermi level of graphene. Transferring another graphene layer on top of monolayer reduces the transmittance of two layer graphene to 95.4% and spin coating TFSA on the top layer shows similar transmittance enhancement to ~100% at all photon energies smaller than the Fermi level of these hybrid graphene layers, as shown in Figure S1 for 50 mM TFSA. Similar transmittance enhancement can also be observed for 3 layer graphene with TFSA doping in Figure S4. However the transmittance saturation is red shifted compared to monolayer graphene/50 mM TFSA. This shift is due to the asymmetric doping on top and bottom layer. Since graphene was doped heavily on top layer by TFSA, the charge flows from top to the bottom graphene (at intrinsic or slightly doped state) to produces a Fermi level equilibrium thus shifting the absorption onset of top towards longer wavelength while the bottom layer towards shorter. Similar phenomenon happens even for three layer graphene doped on top layer. This thus produces a smaller E_F value for the multilayer graphene and thus smaller absorption onset region compared to the monolayer graphene. Here the transmittance of 3 layer graphene is slightly higher than intrinsic value of 93.1% due to the small doping during multiple transfer and heating steps.



S1: Transmittance of mono, bi and tri-layer graphene on quartz substrate before and after 50 mM TFSA doping.

Transmittance from TFSA

Transmittance measurement can be interfered by the chemicals present in the sample. When chemically doped samples are used for measuring optical properties, the intrinsic properties of the doped material can be modified by the absorption bands of doping molecules. Hence use of optically transparent chemical dopants can be an effective solution to obtain intrinsic information from chemically doped samples. TFSA dopant prepared in nitromethane solvent and spin-coated onto quartz substrate at 2000 rpm for 1 minute was observed to be spectrally constant in the entire region of our

interest (Figure S2). This thus gives the transmittance spectra of p-doped graphene without any unnecessary modification from the doping molecules. The slight deviation between 20 mM and 50 mM TFSA in IR range is due to the small noise level in the machine as seen in the quartz spectra. Here the 20 mM and 50 mM spectra were obtained subtracting the quartz background while the spectra of quartz was obtained by subtracting air as the background.



S2: Transmittance of 20 mM and 50 mM TFSA on quartz substrate showing absence of any absorption bands from TFSA within the range of transmittance measurement together with transmittance of quartz substrate.

Extraction of Fermi level from transmittance

The different transmittance profile in region one and two arises from the absorption saturation and onset region as explained in the main text. Absorption saturation continues till the photon wavelength equivalent to lower E_F bound and after which the onset of absorption continues till the lower E_F bound. The interpolation of the two regions denoted by the black dotted lines in Figure S3 and their intersection denoted by the black arrow represent $2E_F$ for 30 mM TFSA doped graphene on quartz substrate. The inset shows the dirac spectrum and the E_F position.



S3: Schematic of the 30 mM TFSA doped graphene showing the E_F extraction process from transmittance. The inset is the Dirac cone showing the Fermi level position.

Transmittance of as prepared and TFSA-doped graphene on various substrates

The SiO₂ substrate has been known to withdraw charges from graphene by O⁻/OH⁻ functional groups.¹⁻² Hence to remove substrate-based doping effect, h-BN has been extensively used as a passivation layer. Figure S4 shows the transmittance spectra of as-prepared and TFSA-doped graphene with monolayer h-BN transferred onto quartz substrates. The absorption onset region and the corresponding Fermi level value (Figure 2b) are lower than graphene on quartz. It can be interpreted that substrate induces doping which modifies the low doping region and finally saturates to a similar value in graphene/quartz with higher doping.

Deeper understanding of these transmittance properties in graphene requires substrates with very small surface roughness, wide optical window, and weak interaction energy. CaF₂ substrate, known to be highly hydrophilic³ possesses all these essential properties. Hence compared to quartz, it gives wide range of transmittance spectra of graphene with negligible fluctuation in FIR regions (Figure S5). Here the absorption onset region and the corresponding Fermi level (Figure 2b) starts saturating at 20 mM TFSA doping due to low substrate-based doping effect.

(a)



S4: Transmittance of MLG under various TFSA doping concentration on h-BN/quartz as a substrate. h-BN has been used as a passivation layer to reduce the substrate interaction.



S5: Transmittance of MLG under various TFSA doping concentrations on CaF₂ substrate with longer wavelength range.

Transmittance of background substrates

Small change in the Fermi level position of graphene can be observed in FIR regions. Quartz substrate which has smaller optical window and a huge absorption peak at 2723 nm (Figure S6) by water molecules⁴ limits the transmittance measurement at FIR region. To overcome these limitations, we used CaF_2 and monolayer h-BN having uniform transmittance in a wide wavelength range to verify the absorption quenching in FIR range. These substrates also have smaller interaction with graphene and hence lower substrate induced doping compared to quartz can be observed.



S6: Wide wavelength transmittance properties of various substrates used for measuring transmittance.

Substrate and environmental effect on as prepared graphene

As mentioned before, substrate and unintentional doping from environment brings variation in pristine graphene properties. To understand this, as-prepared graphene on quartz and h-BN/quartz were prepared by heating overnight at 80°C. Graphene on quartz heated at 80°C for 12 hr shows much higher transmittance than graphene on h-BN/quartz under similar conditions and graphene on quartz measured instantly after transfer (Figure S7). This higher transmittance is due to the combination of substrate and environment doping that affects graphene on quartz, while only environment affects graphene on h-BN/quartz. Here heating at 80 °C assists the faster absorption of gas molecules on graphene.

Unintentional doping in as prepared graphene from oxygen and moisture are slower and changes Fermi level position by much smaller value than substrate-based doping. To observe this small Fermi level shift, CaF₂ having a wide optical window was used as a substrate. The FTIR data (Figure S8b and S8b) shows the transmittance saturation and the absorption onset which follows in the visible region similar to those in TFSA-doped graphene. Heating assisted and air-exposed samples for 12 h shows different absorption onset region from pristine sample (Figure S8). This onset region is redshifted when CaF₂ substrate is passivated with monolayer h-BN (Figure S9). Slightly downshifted and constant spectrum in IR region was observed for samples heated in air at 80 °C for 12 hr. It might be due to the removal of some organic contaminations in graphene which makes graphene spectrally flat and increases reflection in IR region.



S7: Comparison of transmittance saturation of monolayer as-prepared graphene on quartz and h-BN/quartz substrates measured in different environmental conditions.



S8: UV-Visible-IR transmittance of MLG on CaF_2 substrate. (a) UV-visible spectroscopy and (b) FTIR spectroscopy under different environmental conditions.



S9: UV-Visible-IR transmittance of MLG on h-BN/CaF₂ substrate. (a) UV-Visible-IR spectroscopy and (b) FTIR spectroscopy under different environmental conditions. h-BN passivation helps reduce the substrate interaction thus minimizing doping in graphene.

XPS analysis of graphene on various substrates

High resolution C1s spectra of as-prepared monolayer graphene on SiO₂/Si substrate shows four different peaks from the deconvolution of C1s full spectra. The peaks are mainly sp^2 , sp^3 , C-O and C=O groups. The sp^2 and sp^3 spectra are mainly from the carbon bonding in graphene, while C-O are functional groups contributed from the substrate and environmental oxidation and C=O from transfer process (mainly PMMA C4) which are mostly present in CVD graphene⁵⁻⁶ in Figure S10a. In h-BN passivated graphene (Figure S10b), the absence of the C-O peak suggests that either graphene interaction with SiO₂ is completely eliminated, suggesting that the passivation reduces the doping of graphene from the SiO₂ substrate or h-BN reduces the oxidation rate of graphene due to environment and hence the 110 meV shift in binding energy compared to graphene on SiO₂ substrate. Similarly

Figure S10c shows the 50mM TFSA-doped C1s spectra with CF_3 peaks, implying the presence of doping from TFSA. Inset shows the molecular structure of TFSA dopant used.



S10: High resolution C1s XPS spectra of monolayer graphene on various substrates: (a) pristine graphene on SiO₂/Si (b) pristine graphene on h-BN/SiO₂/Si (c) 50 mM TFSA doping on SiO₂/Si. Inset shows the molecular structure of TFSA dopant.

Hall bar analysis of as-prepared and heat treated samples

Variation of Fermi level in graphene occurs due to substrate, unintentional environment doping and strain as explained in the main text. Figure S11 shows the hall bar measurement of as-prepared and same sample heated overnight at 80°C. Linear fitting of Magnetic field *versus* Hall resistance for as-transferred graphene gives a slope of 435.4 showing carrier concentration of 1.43×10^{12} cm⁻². The same sample after annealing at 80°C for 12 hr shows a slope of 77.65, giving a carrier concentration of 8.04×10^{12} cm⁻² which shifts the Fermi level of graphene 360 meV lower in valence band similar to the Fermi level shift of 343 meV extracted from transmittance measurement of pristine graphene on quartz substrate annealed at 80°C for 12 hr. As explained in the transmittance part, this shift might be due to the absorption of gas molecules (especially oxygen and moisture) or due to enhanced surface interaction of graphene at alleviated temperature which is known to p-dope graphene.



S11: Hall bar analysis of as-prepared on SiO₂/Si and same graphene sample annealed at 80° C for 12 hour.

Raman analysis of as prepared and TFSA-doped graphene

Correlation of G and 2D peaks from the statistical analysis of the Raman mapping can provide valuable information on the doping (TFSA doped and unintentional) distribution and strain. Since the doping and strain variations can occur in microscopic scales, Raman analysis of large area graphene can give valuable information on how the doping distribution is changed. Here 50x50 μ m² graphene area is mapped before (at various environmental and substrate conditions) and after TFSA doping. The

various samples doped before and after with different TFSA concentrations are presented systematically in Figure S12 and S13. Doping and the amount of strain on the samples can be analyzed based on the peak shift of G and 2D, FWHM of G and 2D and also the correlation of G and 2D shifts as explained in the main text. Figures S12(a) and (b) shows the histogram of peak shift and FWHM of samples with different doping concentrations. The shift of G band peaks for different as-prepared samples is based on their initial conditions of growth, transfer and environment factors even though they were fabricated on the same conditions. This thus shows that the variation of doping occurs from the pristine sample itself. Based on this, Figure S13a shows the FWHM of G and 2D peak before and after various TFSA doping concentrations which are in line with the previous literatures where the FWHM of G and 2D peak decreases with doping concentration. Similarly based on the displacement of G peak position by 35.4 cm⁻¹/eV of E_F shift and -69.1 cm⁻¹/% of biaxial strain, Figure S13b shows the Fermi level shift and percentage of strain calculated for same samples before and after doping. The variation of doping in pristine samples as like in FWHM analysis can also be seen here. It is also evident from the E_F value that strain is also important parameter in analyzing E_F for low doped samples. Figure S13c shows the same results in terms of different doping concentration. Similarly the doping variation due to environmental effects and substrate has been extracted from Raman maps carried out for as-prepared graphene sample exposed in air and a sample heated at 80°C (both SiO₂/Si substrate) and a sample on the substrate passivated by h-BN (Figure S14a-d). The average spectra from the mapping region are shown in Figure S14e. Based on the correlation analysis of G and 2D band shift (same as for Figure 5 of the main text), the strain and the E_F shift were obtained for each pixel of the Raman map, corresponding to different spots of the sample. Figure S14f shows correlation between the strain and doping level for as prepared samples on SiO_2/Si (blue), air exposed for 12 hours (green) and annealed further at 80°C for 12 hours (brown) w.r.t the as transferred sample on h-BN passivated SiO₂/Si (red). The E_F shift values of pristine and air exposed samples, offset w.r.t. the h-BN passivated sample, are 70 and -66 meV, while 80°C heat treated sample showed insignificant difference in doping compared to the h-BN passivated sample, although much broader distribution. That sample also

showed the largest strain values among those samples. We conclude that the air exposure produces environmental effect and heat treatment likely compensates for this effect, though also increases strain.



S12: Histogram plot of the Raman mapping data of graphene before (blue) and after (red) TFSA doping showing the variation of (a) G (left) and 2D (right) frequency shift (b) FWHM value of G (left) and 2D (right) before (green) and after (orange) TFSA doping.



S13: Raman analysis of the mean data obtained from mapping: (a) FWHM for G and 2D peak before and after TFSA doping. (b) Fermi level shift before (blue) and after (gray) TFSA doping (upper panel) and strain before (orange) and after (red) TFSA doping (bottom panel). (c) The Fermi level value and the corresponding strain obtained for same samples before and after TFSA doping.

S14: Raman mapping of G (top) and 2D (bottom) peak position of $50 \times 50 \text{ um}^2$ as-prepared graphene on various substrates under different environmental conditions: (a) as prepared on SiO₂/Si (labeled in blue in panel (f)), (b) air-exposed for 12 hours on SiO₂/Si (green), (c) heated at 80°C for 12 hours on SiO₂/Si (brown), and (d) as-transferred on h-BN/SiO₂/Si (red). Panel (e) shows the average Raman spectra of the whole mapping area while panel (f) presents Fermi Energy level and the strain values calculated for different substrates and environmental conditions using 35.4 cm⁻¹/eV of Fermi level shift and -69.1 cm⁻¹/% of biaxial strain shift. Partial distribution functions for E_F are shown in panel (g) with the same color code.

Notes and references

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