

Intercalation of Few-Layer Graphite Flakes with FeCl₃: Raman Determination of Fermi Level, Layer by Layer Decoupling, and Stability

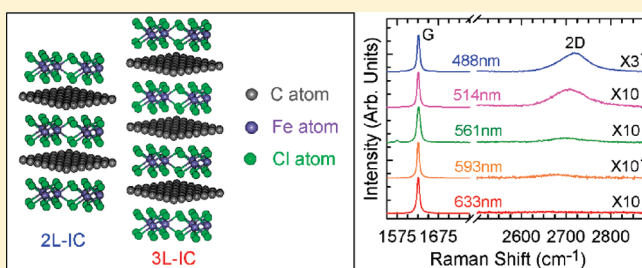
Weijie Zhao,[†] Ping Heng Tan,^{*,†} Jian Liu,[†] and Andrea C. Ferrari[‡]

[†]State Key Laboratory for Superlattices and Microstructures, Institute of Semiconductors, Chinese Academy of Sciences, Beijing 100083, China

[‡]Department of Engineering, University of Cambridge, Cambridge CB3 0FA, United Kingdom

S Supporting Information

ABSTRACT: We use anhydrous ferric chloride (FeCl₃) to intercalate graphite flakes consisting of 2–4 graphene layers and to dope graphene monolayers. The intercalant, staging, stability, and doping of the resulting intercalation compounds (ICs) are characterized by Raman scattering. The G peak of heavily doped monolayer graphene upshifts to ~ 1627 cm⁻¹. The 2–4 layer ICs have similar upshifts, and a Lorentzian line shape for the 2D band, indicating that each layer behaves as a decoupled heavily doped monolayer. By performing Raman measurements at different excitation energies, we show that, for a given doping level, the 2D peak can be suppressed by Pauli blocking for laser energy below the doping level. Thus, multiwavelength Raman spectroscopy allows a direct measurement of the Fermi level, complementary to that derived by performing measurements at fixed excitation energy significantly higher than the doping level. This allows us to estimate a Fermi level shift of up to ~ 0.9 eV. These ICs are thus ideal test-beds for the physical and chemical properties of heavily doped graphenes.



Graphite intercalation compounds (GICs) have atomic or molecular layers inserted between the graphene sheets.^{1,2} They have been intensively studied because of novel features in their structural, electronic, and optical properties.^{1–8} They are promising for electrodes, conductors, superconductors, catalysts, hydrogen storage, batteries, displays, and polarizers.^{1–6,8} Since their first synthesis in 1841,⁹ hundreds of GICs have been produced with a variety of reagents acting as donor and acceptor intercalants.^{1,2} Staging is the most characteristic property of GICs. This consists of intercalate layers periodically arranged in a matrix of graphene layers. The resulting GICs are designated in terms of a staging index *n*, which denotes the number of graphene layers between adjacent intercalate layers.¹ Thus, *e.g.*, in stage-1 GICs, each graphene layer is sandwiched by two intercalant layers;^{1–4,6} in stage 2, the intercalant layers sandwich two graphene layers,^{1,4} and so on. However, it is difficult to manipulate and process traditional GICs into nanoelectronic devices due to their thickness.^{1,2} Graphene has great potential in nanoelectronics and optoelectronics.^{10,11} By intercalating graphite flakes just a few layers thick, one can combine the physical and chemical properties of GICs with those of single-layer (SLG) and few-layer graphene (FLG) and open new opportunities for applications in nanoelectronics.^{12–21} There is also great interest in the transport properties of graphene at high carrier density, both for applications and for fundamental physics.^{12,13,17–19} By means of an electrolytic gate, refs 12,13,

and 18 doped graphene up to $\sim 4.5 \times 10^{13}$ cm⁻². Reference 19 used an ionic-liquid gate to achieve a carrier density higher than 10^{14} cm⁻². Reference 17 achieved 4×10^{14} cm⁻² for hole and electron doping by means of solid polymer electrolytes. We note that in donor-type graphite intercalation compounds, such as KC₈, the electron density can reach up to $\sim 4.8 \times 10^{14}$ cm⁻², corresponding to a Fermi shift of ~ 1.3 eV.^{1,6,7} There is thus scope for using a similar approach to achieve graphene doped at levels higher than those reported in refs 6,12,13, and 17–19.

Here, we use FeCl₃ to intercalate FLG flakes into stage-1 GICs. Raman spectroscopy at several wavelengths monitors the resulting material. This shows the formation of acceptor-type stage-1 GICs. We estimate a Fermi shift of ~ 0.9 eV, corresponding to a fractional charge transfer of $\sim 1/6.6 = 0.152$ holes per carbon atom,^{1,3} *i.e.*, a hole density of $\sim 5.8 \times 10^{14}$ cm⁻².

Graphite flakes consisting of 1–4 layers (L) are obtained by micromechanical cleavage of natural graphite on a Si+300 nm SiO₂ substrate.²² The number of layers is identified by optical contrast^{23,24} and atomic force microscopy (AFM),²² as shown in Figure 1a,b. The Raman spectra are taken at room temperature using a Jobin-Yvon HR800 system with a ~ 1.2 cm⁻¹ spectral resolution. Intercalation is performed following the vapor transport method commonly used in GICs, as discussed, *e.g.*,

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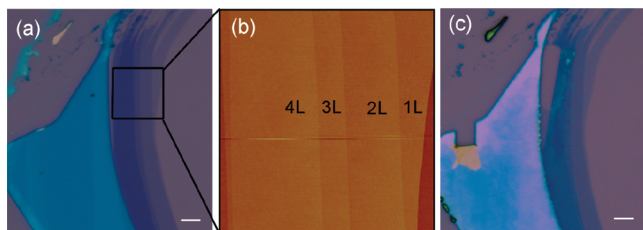


Figure 1. (a) Optical image of a pristine 1–4 L flake. (b) AFM image of the region indicated in (a) by a solid square. (c) Optical image after FeCl_3 doping/intercalation. The scale bar in (a) and (c) is $4 \mu\text{m}$.

in ref 1. The intended intercalant and the flakes are positioned in different zones in a glass tube, as shown in Figure 5b of ref 1. The glass tube is pumped to $\sim 1.5 \times 10^{-4}$ Torr and kept at 393 K for more than one-half an hour to ensure FeCl_3 is anhydrous. Next, it is sealed and inserted in an oven with a reaction temperature of 613K for 6 and 30 h, for SLG/FLG and bulk graphite, respectively. This is different from the traditional two-zone method reported, *e.g.*, in Figure 5b of ref 1, where the graphite and FeCl_3 are at different temperatures. Note that a longer reaction time is needed to reach stage-1 GIC for bulk graphite, due to the sample size, both in spatial extent and in thickness. The glass tube is then taken out of the oven. The samples are exposed to air following two procedures. In the first, they are immediately removed from the still hot glass tube. In the second, the glass tube is first air-cooled to room temperature while still sealed, then the samples are removed. Figure 1c shows an optical micrograph of a representative intercalated flake. The number of layers can still be identified, because the contrast is higher than prior to intercalation.

In GICs only a few layers thick, it is difficult to apply X-ray diffraction, unlike for bulk GICs staging determination,^{1–4} because of the small thickness and the resulting substrate effects. Raman scattering was used to monitor intercalation and adsorption of bromine (Br_2), iodine (I_2), FeCl_3 , and sulfuric acid.^{25–27} In principle, for stage-1 GICs, a single G peak is expected.^{1–4} However, multiple G peaks were also reported.²⁶

The Raman spectrum of graphene consists of a set of distinct peaks. The G and D appear around 1580 and 1350 cm^{-1} , respectively. The G peak corresponds to the E_{2g} phonon at the Brillouin zone center. The D peak is due to the breathing modes of six-atom rings and requires a defect for its activation.^{28–30} It comes from TO phonons around the K point,^{28,29,31} is active by double resonance (DR),³⁰ and is strongly dispersive with excitation energy due to a Kohn Anomaly at K.³² DR can also happen intravalley, *i.e.*, connecting two points belonging to the same cone around K (or K'). This gives the so-called D' peak, which is at $\sim 1620 \text{ cm}^{-1}$ in defected graphite measured at 514 nm .³⁵ For a given number of defects, the D' intensity is much smaller than the D, due to the smaller electron–phonon-coupling.³² The 2D peak is the second order of the D peak. This is a single peak in SLG, whereas it splits in four in bilayer graphene (BLG), reflecting the evolution of the band structure.³⁶ Raman spectroscopy allows monitoring of doping, defects, strain, disorder, chemical modifications, edges, and relative orientation of the graphene layers.^{12,13,28,32,36–46} Each Raman peak is characterized by position, width, height, and area. The frequency-integrated area under each peak represents the probability of the whole process.⁴⁷ We thus consider both area, $A(2D)/A(G)$, and height, $I(2D)/I(G)$, ratios. In principle, these should show a similar

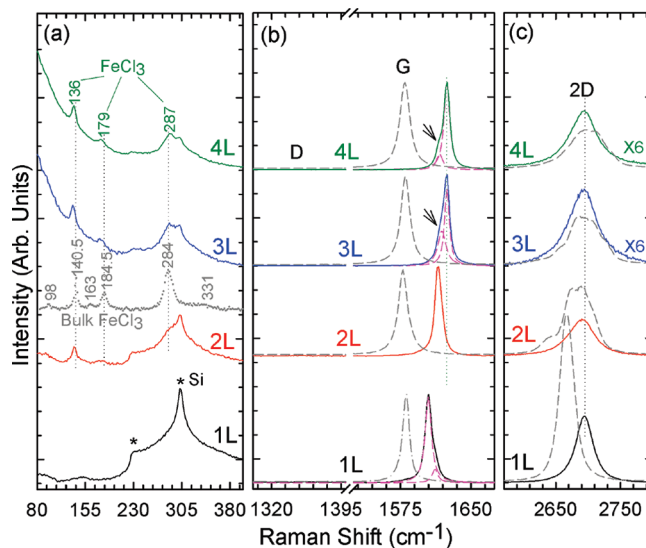


Figure 2. Raman spectra of pristine (dashed lines) and doped/intercalated (solid lines) 1–4 L flakes after exposure to air from the air-cooled glass tubes, measured for 532 nm excitation: (a) low frequency region; (b) D- and G-band region; and (c) 2D-band region. In (a), we also report the Raman spectrum of bulk FeCl_3 (dotted gray line) for comparison. Note the fitted G peak shoulder in 1 L and 3–4 L flakes. Vertical dotted lines are guides to the eye.

behavior. Any discrepancy can be taken as an indication of disorder-induced broadening, because $A(2D)/A(G)$ encompasses both trends of $I(2D)/I(G)$ and $\text{FWHM}(2D)/\text{FWHM}(G)$, where FWHM is the full width at half-maximum.

The G peak position, $\text{Pos}(G)$, has been widely used to identify staging.^{1–4} In graphene, the shift of the Fermi energy has two major effects: (1) a change of the equilibrium lattice parameter, with a consequent stiffening/softening of the phonons,^{12,13,48} and (2) the onset of effects beyond the adiabatic Born–Oppenheimer approximation, which modify the phonon dispersion close to the Kohn anomalies (KAs).^{12,13,32,37,47,49,50} Effect (2) always results in a G upshift, both for electron and hole doping,^{32,37} while (1) gives an upshift for p doping and a downshift for n doping.^{12,13,48} Thus, for low doping levels, below $\sim 3 \times 10^{13} \text{ cm}^{-2}$, both n and p doping result in G peak upshifts,^{12,13,48} but for levels above $\sim 3 \times 10^{13} \text{ cm}^{-2}$,⁵⁰ the n doped case reverses. In fact, for n doping of $\sim 10^{14} \text{ cm}^{-2}$, the G shift would revert to zero.⁵⁰

The procedure followed to remove GIC samples from the glass tubes can strongly affect their doping level. We first consider the Raman spectra of 1–4 L flakes exposed to ambient air, after the sealed glass tubes are cooled to room temperature; see Figure 2.

FeCl_3 has eight Raman-active modes $4A_g + 4E_g$ ($2A_{1g} + 2A_{2g} + 4E_g$).³ Six of them ($3A_g + 3E_g$) have been measured so far.³ When FeCl_3 was used as intercalant in stage-1 GICs, only four Raman modes, $2A_{1g}$ and $2E_g$, were observed,³ at 93 cm^{-1} (denoted as $E_g(L)$), 139 cm^{-1} (denoted as $A_{1g}(L)$), 181 cm^{-1} (denoted as $E_g(H)$), and 287 cm^{-1} (denoted as $A_{1g}(H)$). The other two A_g and E_g modes at 164 and 354 cm^{-1} are probably too weak to be observed in GICs. Indeed, even in bulk FeCl_3 , those modes are very weak.³ Figure 2a shows that, after doping by FeCl_3 , three Raman modes from FeCl_3 are observed in the low frequency region: $A_{1g}(L)$ at 136 cm^{-1} , $E_g(H)$ at 179 cm^{-1} , and $A_{1g}(H)$ at 287 cm^{-1} . We cannot detect the other $E_g(L)$ mode at

$\sim 93 \text{ cm}^{-1}$, because this is too weak to be distinguished from the background. These peak positions differ from those of bulk crystalline FeCl_3 , whose spectrum is also shown in Figure 2a for comparison: the $A_{1g}(\text{L})$ and $E_g(\text{H})$ modes have a $\sim 4 \text{ cm}^{-1}$ downshift, while the $A_{1g}(\text{H})$ mode upshifts $\sim 3 \text{ cm}^{-1}$. The $A_{1g}(\text{L})$ and $E_g(\text{H})$ downshift and $A_{1g}(\text{H})$ upshift as compared to bulk FeCl_3 agree with previous reports^{1,3} and further validate the intercalation process. In bulk FeCl_3 , the iron layer is sandwiched by two chlorine layers, as shown in Figure 1 of ref 3. When intercalation happens, chlorine atoms simultaneously occupy preferred sites associated with the graphene lattice, which results in the loss of the Cl atoms long-range two-dimensional order, because their in-plane structure is incommensurate with the graphene host lattice.^{1,3} Fe atoms, however, retain the long-range order as in crystal FeCl_3 .^{1,3} This results in a $\sim 3^\circ$ relative rotation of the Cl layers above and below the Fe layer, and a difference of the Raman modes of intercalated FeCl_3 as compared to bulk FeCl_3 .^{1,3} FeCl_3 modes are not observed in the FeCl_3 -doped SLG in Figure 2a due to the very low density of FeCl_3 on the SLG surfaces, when compared to fully- FeCl_3 -intercalated GICs, probably due to desorption.

Figure 2 plots the Raman spectra of 1–4 L flakes measured at 532 nm before (dashed lines) and after (solid lines) FeCl_3 intercalation. The pristine samples have the characteristic features of mono- and multilayer graphene, as previously reported.^{27,36,39} The change in $\text{Pos}(\text{G})$ for doped/intercalated samples as compared to pristine ones in Figure 2b is a signature of doping. The blueshift is smaller in SLG as compared to FLG. This indicates fewer FeCl_3 molecules on SLG relative to 2–4 L flakes. The SLG 2D band in Figure 2c upshifts $\sim 28 \text{ cm}^{-1}$, typical of hole-doping,^{12,13} while $I(2\text{D})/I(\text{G})$ and $A(2\text{D})/A(\text{G})$ decrease $\sim 61\%$ and $\sim 53\%$ relative to those prior to doping. From refs 13 and 47, we estimate the Fermi shift of SLG to be $\sim 0.4 \text{ eV}$. The 2D line shape for the 2–4 L flakes after FeCl_3 intercalation changes significantly, as shown in Figure 2c, from multiple peaks into a single Lorentzian. This is an indication of electronic decoupling of the layers.^{36,39} Note that the presence of any nonintercalated BLG or FLG would give residual multiple 2D bands. In pristine Bernal-stacked graphite, the interlayer distance is 3.35 \AA .^{1,2} When FeCl_3 molecules are intercalated, the distance increases to 9.37 \AA .^{1–4} As a result, the interlayer interaction significantly decreases.^{1,2,6} Therefore, the single Lorentzian 2D peak indicates SLG between two intercalant layers, each SLG being hole-doped.

As shown in Figure 2b, the G bands of SLG and BLG are at ~ 1605 and $\sim 1615 \text{ cm}^{-1}$, moving to $\sim 1625 \text{ cm}^{-1}$ for 3 and 4 L. The latter value is close to that previously reported ($\sim 1626 \text{ cm}^{-1}$) in FeCl_3 stage-1 GICs.^{1–4} For 3 and 4 L, an additional sideband appears at $\sim 1618 \text{ cm}^{-1}$, with almost equal width to the main peak. One might be tempted to assign this band to the D' peak activated by defects.^{33,34} However, in graphene, graphite, and nanotubes, the electron–phonon coupling is maximum for the TO branch around K ,^{32,50–52} so that, in the presence of defects, the intensity of the activated D peak is higher than the D' peak.^{35,42,53} Here, the D peak intensity is unobservable for all the layers, before and after doping/intercalation, as shown in Figure 2b. Also, the sideband at $\sim 1618 \text{ cm}^{-1}$ is not always observed in all of the intercalated/doped flakes. Therefore, it is not the D' peak. This band is thus another G peak, resulting from nonuniform intercalation, due to desorption of FeCl_3 following exposure to air. Indeed, we observe multiple G peaks in GICs with nonuniform intercalation (see the

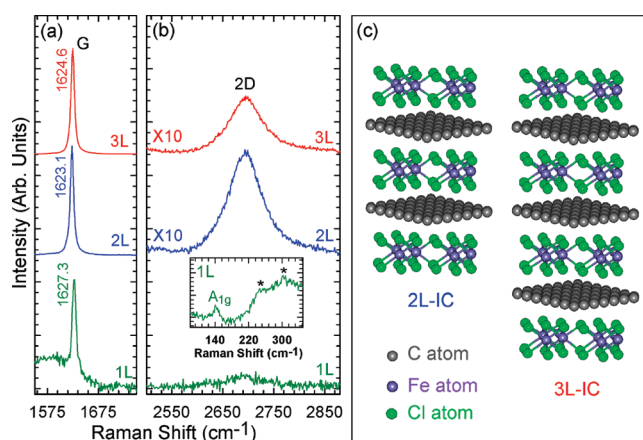


Figure 3. (a) G band and (b) 2D band of stage-1 2–3 L flakes exposed to air from the hot glass tube, and of doped SLG sealed in an air-cooled glass tube. The excitation wavelength is 532 nm. The inset shows the spectrum of the doped SLG in the low frequency region. Stars indicate features due to the Si substrate. (c) Schematic illustrations of fully- FeCl_3 -doped/intercalated 2–3 L flakes.¹

Supporting Information). Similarly to that previously observed for H_2SO_4 -doped flakes,²⁷ FeCl_3 desorption from the outer surface of the top layer is assumed to be much easier than from the bottom layer close to the substrate. Thus, the top layer of doped 3–4 L flakes mostly contributes to the low-frequency peak. The thicker are the flakes, the less the top layers contribute to the overall Raman intensity. Indeed, 4 L flakes have weaker relative intensity of this shoulder, as compared to the main G peak, than the 3 L flakes. We note that no shoulder is observed for the doped/intercalated BLG, indicative of homogeneous doping. In SLG we sometimes observe a weak shoulder at $\sim 1612 \text{ cm}^{-1}$, as in Figure 2b. However, such shoulder is position dependent and not always seen (see the Supporting Information). Thus, this is due to inhomogeneous doping, resulting from low FeCl_3 coverage.

We now consider what happens if the samples are immediately exposed to air from the hot glass tube. In this case, the Raman spectra of intercalated 2–3 L are very similar to those previously reported for stage-1 GICs,^{1–4} as shown in Figure 3a. The single Lorentzian 2D peaks in intercalated 2–3 L flakes indicate the formation of stage-1 intercalation compounds. The G band of FeCl_3 -intercalated 2–3 L can be fitted by a single Lorentzian, with no sidebands. This again shows that the doping of each graphene layer in the flake is uniform. The 2–3 L flakes directly exposed to air from the hot glass tubes exhibit a more uniform doping and a higher doping level than those exposed to air from the air-cooled glass tubes. This suggests that the FeCl_3 -doped FLGs are more stable in air than in vacuum, similar to what was reported in previous studies of bulk GICs.^{1,54} Figure 3a, b indicates that $\text{Pos}(\text{G})$ for BLG is slightly lower than in 3 L flakes, and $I(2\text{D})/I(\text{G})$ for BLG is higher than in 3 L flakes. This points to deintercalation in these BLGs.

Let us consider the outer surfaces of the top and bottom layers of intercalated 2–4 L flakes. If FeCl_3 is only present on a single (inner) side of these layers, we expect the amount of charge transfer to reach at most that of stage-2 GICs. In this case, the corresponding $\text{Pos}(\text{G})$ can only shift to $\sim 1612 \text{ cm}^{-1}$, *i.e.*, $\text{Pos}(\text{G})$ of FeCl_3 -intercalated stage-2 GICs.^{1–4} In Figure 2, the $\text{Pos}(\text{G})$ of our FeCl_3 -doped 2 L flakes is $\sim 1615 \text{ cm}^{-1}$, very close

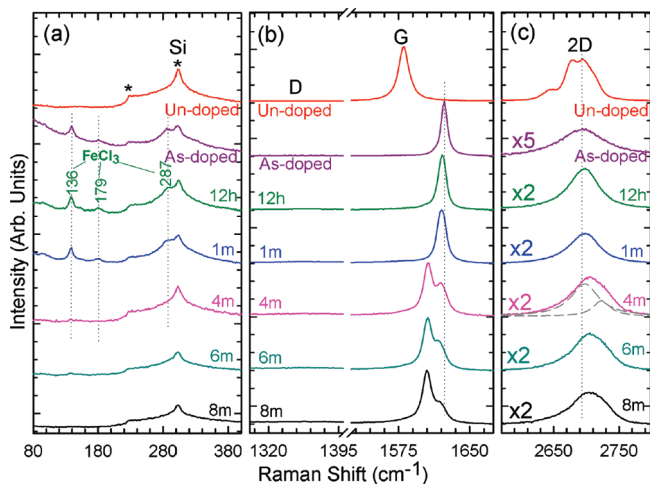


Figure 4. Raman spectra of as-prepared 2 L-GICs exposed to air from the hot glass tube, and after 12 h, and 1, 4, 6, and 8 months: (a) low frequency region; (b) D and G band region; and (c) 2D band region. The excitation wavelength is 532 nm. A pristine 2L is also included as reference. The 2D band of 2 L-GICs after 4 months is fitted by two Lorentzians. Vertical dotted lines are a guide to the eye.

to that ($\sim 1612 \text{ cm}^{-1}$) reported in ref 26, where double G peaks, at ~ 1612 and $\sim 1623 \text{ cm}^{-1}$, were also observed for 3 and 4 L samples. Reference 26 argued that FeCl_3 does not adsorb on the top and bottom of their flakes. We note that Pos(G) of the lower energy G band in our 3–4 L FeCl_3 -intercalated flakes ($\sim 1618 \text{ cm}^{-1}$) is higher than previously reported for FeCl_3 intercalated stage-2 GICs.^{1–4} Furthermore, in Figure 3, Pos(G) of intercalated 2–3 L is ~ 1623 and $\sim 1625 \text{ cm}^{-1}$, much larger than $\sim 1615 \text{ cm}^{-1}$ in Figure 2 and $\sim 1612 \text{ cm}^{-1}$ observed for stage-2 GICs.^{1,4,25} Therefore, we argue that the top and bottom layers of our FeCl_3 -intercalated 2–4 L have double-face doping. In the case of the 2–4 L flakes in Figure 2, the top layers are not with full coverage, due to FeCl_3 desorption, unlike the inner layers.

The doping of SLG is via adsorption of FeCl_3 molecules. No matter the procedure we used, the G peak of FeCl_3 -doped SLG is located at $\sim 1605 \text{ cm}^{-1}$, similar to Figure 2. However, when measuring in situ Raman spectrum of doped SLG still sealed in the air-cooled glass tube, Pos(G) reaches $\sim 1627 \text{ cm}^{-1}$, Figure 3a, indicative of heavy doping. This value is much higher than in ex situ measurements. This would point to doped-SLG being more stable in the sealed glass tube, contrary to what we observe for doped 2–4 L flakes. A broad $\text{FeCl}_3 \text{ A}_{1g}$ peak with $\text{FWHM} \sim 16 \text{ cm}^{-1}$ appears at $\sim 142 \text{ cm}^{-1}$ in the in situ spectra, indicative of adsorbed FeCl_3 . The autodissociation of FeCl_3 can provide chlorine gas.¹ Although chlorine cannot be intercalated into graphite,¹ the residual gas can adsorb on the SLG surface and dope it. A similar effect happens with bromine, as discussed in ref 25. The effect of such chlorine-induced doping is less in the case of FLG, due to the presence of several non surface-exposed graphene layers, even more so for the usual GIC structures. In the sealed glass tube, FeCl_3 is definitely adsorbed on SLG, as indicated by FeCl_3 modes. However, the frequency of these modes is closer to those of bulk FeCl_3 . When the doped SLG is exposed to air, the volatilization of the adsorbed chlorine and FeCl_3 desorption result in lower doping, as compared to FLG in air.

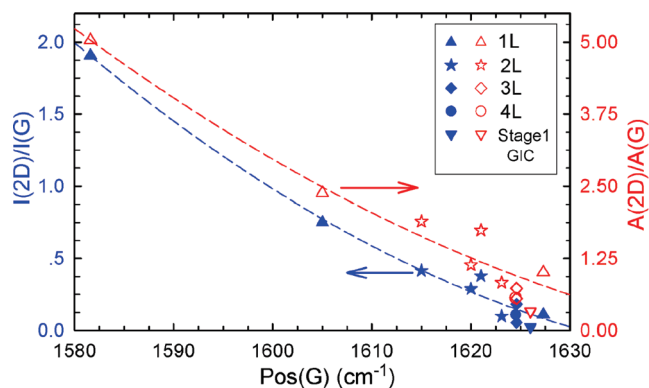


Figure 5. Variation of $I(2D)/I(G)$ and $A(2D)/A(G)$ as a function of Pos(G) . The blue and red dashed lines are guides to the eye.

To further study the desorption/deintercalation, Figure 4a–c reports the BLG Raman spectra as a function of time for a period of up to 8 months. Pos(G) starts at $\sim 1623 \text{ cm}^{-1}$ and can be fitted with a single Lorentzian with $\text{FWHM(G)} \approx 8 \text{ cm}^{-1}$, indicating uniform doping.^{12,13,37,41} After 12 h, Pos(G) decreases to $\sim 1621 \text{ cm}^{-1}$ and FWHM(G) increases to $\sim 10 \text{ cm}^{-1}$. After 1 month, $\text{Pos(G)} \approx 1620 \text{ cm}^{-1}$ and $\text{FWHM(G)} \approx 12 \text{ cm}^{-1}$. This indicates that FeCl_3 -intercalated flakes are relatively stable in air at room temperature for up to 1 month. The intercalant Raman modes change little within 1 month. However, after 4 months they are not seen anymore, while G and 2D acquire a multiple peak profile, Figure 4c. The appearance of multiple G peaks may result from different desorption on different layer surfaces. Indeed, the intensity of the intercalant Raman mode at $\sim 136 \text{ cm}^{-1}$ significantly decreases after 1 month. After 8 months, the mode is unobservable.

Figure 5 plots $I(2D)/I(G)$ and $A(2D)/A(G)$ as a function of Pos(G) . With increasing Pos(G) , *i.e.*, increasing doping, $I(2D)/I(G)$ and $A(2D)/A(G)$ both decrease. $I(2D)/I(G)$ and $A(2D)/A(G)$ of some intercalated 2–4 L flakes are close to that of GICs, further confirming that 2–4 L flakes can be full-doped by FeCl_3 via adsorption on surface layers and intercalation into inner layers.

We now consider the dependence of $I(2D)/I(G)$ and $A(2D)/A(G)$ on doping and excitation wavelength. We use a FeCl_3 -intercalated stage-1 GIC as an example to show how to probe the Fermi level by multiwavelength Raman spectroscopy, because in this case the Fermi energy (E_F) is well known by independent characterizations.¹ Figure 6a shows the Raman spectra measured at 488, 514, 561, 593, and 633 nm. These are similar to those in Figure 3. $\text{Pos(G)} \approx 1626 \text{ cm}^{-1}$ for all lasers, $\text{FWHM(G)} \approx 7 \text{ cm}^{-1}$, in good agreement with what was previously reported for FeCl_3 -intercalated stage-1 GICs.^{1–4} At 633 nm, the 2D peak is almost unobservable, similarly to what was reported in ref 25 for SLGs doped by bromine. However, increasing the excitation energy from 2.09 eV (593 nm) to 2.54 eV (488 nm), the 2D peak appears with a Lorentzian line shape, a typical behavior of heavily doped SLG. $A(2D)/A(G)$ and $I(2D)/I(G)$ are plotted as a function of excitation energy in Figure 6b. The trend of these intensity ratios can be understood considering the Raman scattering process for the 2D band.^{47,49} Figure 6c plots the doped SLG band structure. For a given laser energy, to activate the 2D peak, an electron–hole pair must be excited in process $a \rightarrow b$, and recombined in process $c \rightarrow d$. These transitions differ by the 2D peak energy:

$$E_T = E_L - \hbar\omega_{2D} \quad (1)$$

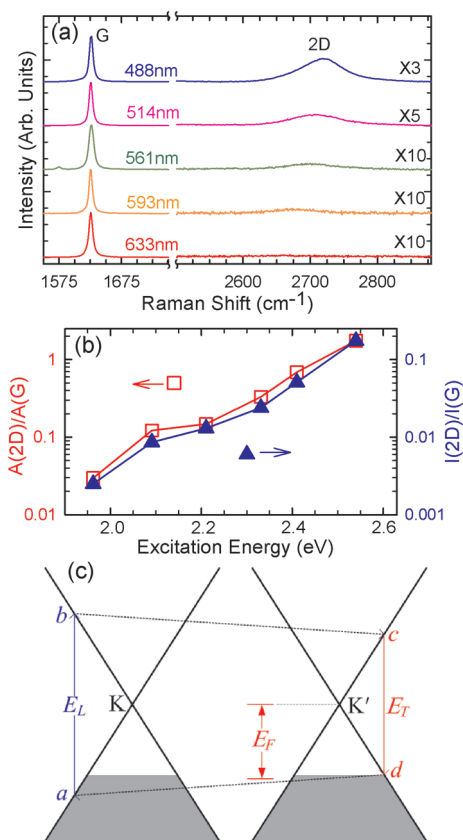


Figure 6. (a) Raman spectra of stage-1 GIC measured at 488, 514, 532, 561, 593, and 633 nm, normalized to have the same $I(G)$. (b) $A(2D)/A(G)$ and $I(2D)/I(G)$ as a function of excitation energy. (c) Schematic diagram of the band structure and Raman processes for the 2D band: $a \rightarrow b$, photon absorption; $c \rightarrow d$, electron–hole recombination; $b \rightarrow c$ and $d \rightarrow a$, phonon emission.

where E_L , E_T , and ω_{2D} are the excitation energy, the energy corresponding to electron–hole recombination process $c \rightarrow d$, and the 2D frequency. There are three cases: (1) When E_L and E_T are both larger than $2E_F$, the 2D band can be always observed; (2) when E_L is larger than $2E_F$, but E_T is smaller than $2E_F$, process $c \rightarrow d$ is forbidden due to Pauli blocking; and (3) when both E_L and E_T are smaller than $2E_F$, both processes $a \rightarrow b$ and $c \rightarrow d$ are forbidden. Therefore, only when $E_T > E_L$, i.e., $(E_L - \hbar\omega_{2D})/2 > E_F$, the 2D band is observable. Thus, the absence of the 2D band in the Raman spectra of FeCl_3 -intercalated stage-1 GICs, and FeCl_3 , Br_2 , and H_2SO_4 heavily doped SLGs^{25,27} at 1.96 eV (633 nm), indicates that their E_F should be larger than 0.81 eV. When $(E_L - \hbar\omega_{2D})/2 > E_F$, both $I(2D)/I(G)$ and $A(2D)/A(G)$ should increase. Thus, by considering the sharp intensity increase when moving from 2.09 eV (593 nm) to 1.96 eV (633 nm), we can estimate that the transition energy corresponding to the excitation energy of 2.02 eV is close to $2E_F$. Therefore, $E_F \approx 0.85$ eV, close to ~ 0.9 eV measured in stage-1 GICs by electron energy loss spectroscopy.¹

Reference 47 derived a simple equation, valid for excitation energy above the Fermi energy, linking doping to $A(2D)/A(G)$ as:

$$\sqrt{\frac{A(G)}{A(2D)}} = \frac{C}{\gamma_{e-ph}} [\gamma_{e-ph} + |E_F| f(e^2/2\epsilon_0\epsilon h\nu_F)] \quad (2)$$

where γ_{e-ph} , E_F , e , ϵ_0 , ϵ , h , and ν_F are the scattering rate due to the emission of phonons, Fermi energy, electron charge, permittivity of vacuum, dielectric constant, Planck constant, and electron velocity.⁴⁷ C is a constant, which was obtained as 0.26 in ref 47 for 514 nm excitation. The numerical values of $f(e^2/2\epsilon_0\epsilon h\nu_F)$ can be taken from Figure 3 in ref 47, and $\gamma_{e-ph} \approx 21$ meV can be extracted from the hole-doping data of ref 13 measured at 514 nm. While ϵ is not available for intercalated FeCl_3 , we can estimate it from that measured for FeCl_3 in aqueous solutions (see the Supporting Information). This gives $f \approx 0.09$. Next, inserting $A(2D)/A(G) \approx 0.7$ in eq 2 gives $E_F \approx 0.84$ eV, very close to that derived by the intensity transition as a function of excitation energy.

In conclusion, graphite flakes consisting of a few graphene layers can be doped by adsorption and intercalation of FeCl_3 . This results in each of the layers behaving as a hole-doped SLG. These are stable up to 1 month after air exposure. The variation of the 2D intensity relative to the G peak with excitation energy allows one to assess the Fermi energy. We estimate $E_F \approx 0.9$ eV, corresponding to a fractional charge transfer of $\sim 1/6.6 = 0.152$ holes per carbon, i.e., $\sim 5.8 \times 10^{14} \text{ cm}^{-2}$, larger than the $\sim 4 \times 10^{14} \text{ cm}^{-2}$ recently reported by employing a solid polymer electrolyte gate.¹⁷

■ ASSOCIATED CONTENT

S Supporting Information. Multiple G peaks resulting from nonuniform doping in graphite. Doping uniformity of FeCl_3 -doped/intercalated 1–4 L flakes. Estimation of FeCl_3 dielectric constant. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

phtan@semi.ac.cn

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