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Forming Weakly Interacting Multilayers of Graphene Using Atomic Force Microscope Tip Scanning and Evidence of Competition between Inner and Outer Raman Scattering Processes Piloted by Structural Defects

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ABSTRACT: We report on an alternative route based on nanomechanical folding induced by an AFM tip to obtain weakly interacting multilayer graphene (wi-MLG) from a chemical vapor deposition (CVD)-grown single-layer graphene (SLG). The tip first cuts and then pushes and folds graphene during zigzag movements. The pushed graphene has been analyzed using various Raman microscopy plots—\(A_2/\Gamma_0 \times E_2^\pm\) vs \(\Gamma_0\), \(\omega_{\text{2D}}\) vs \(\Gamma_2\), \(\Gamma_0\) vs \(\omega_{\text{2D+/-}}\), \(\Gamma_0\) vs \(\Gamma_2\), \(\omega_{\text{2D+/-}}\) vs \(\Gamma_0\), \(\omega_{\text{2D+/-}}\) vs \(\Gamma_2\), \(\omega_{\text{2D+/-}}\) vs \(\Gamma_2\), and \(A_{\text{2D}}/\Gamma_0\) vs \(A_{\text{2D}}/\Gamma_0\). We show that the SLG in-plane properties are maintained under the folding process and that a few tens of graphene layers are stacked, with a limited number of structural defects. A blue shift of about 20 cm\(^{-1}\) of the 2D band is observed. The relative intensity of the 2D\(_{\perp}\) and 2D\(_{\parallel}\) bands has been related to structural defects, giving evidence of their role in the inner and outer processes at play close to the Dirac cone.

Since its first fabrication in 2004,1 single-layer graphene (SLG) has been widely studied. Many efforts have been done to synthesize it,2 developing characterization techniques to understand how atomic structure and defects affect phonons and electrons, which themselves drive heat and electronic transport properties.3 The main effects arise from the Dirac points at the K point in the Brillouin zone (BZ), where the \(\pi\) and \(\pi^*\) bands cross linearly at the Fermi level, forming the so-called Dirac cones that lead the electrons to behave as massless particles with a Fermi velocity reported as high as \(\sim 300\) times lower than the speed of light in vacuum. Changing in a controlled way the behavior of these electrons (by band gap opening, Fermi velocity tuning4,5 etc.) is a major concern for the future of nanoelectronics,6 strain engineering,7 and sensing applications.8

Graphenic family members also inherit some of the astounding properties of graphene planes, such as graphite, amorphous carbon, nanotubes, nanocones, nanoribbons, graphene oxides, etc. Among this family, three-dimensional porous networks of planar graphene9 have been recognized to play an important role in the forthcoming technologies.10,11 It has been shown recently that topology, curvature, and pore properties lead to changes in the electronic and vibrational structures12 or that introducing distortions by hole doping influences the density of states at the Fermi level. Stable Z-shape folded graphene produced using an AFM tip has been observed very recently13,14 opening the area of kirigami/origami of graphene.15 Tailoring the three-dimension architecture of graphene is a key point in controlling some of its properties,16 and the formation of multilayer graphene (MLG) is of importance for this purpose. It has been shown that the number of layers and the way that they are stacked deeply modify the nature of the charge carrier and, therefore, the electronic properties.17 MLGs have already been used for many applications; for example, added to metal oxides in highly sensitive sensors allows the working temperature to be diminished.18 Due to the ability of controlling its lateral size during synthesis, MLG is also a material of choice for...
interacting with biological materials. Several production methods have been used in the past, such as classical mechanical cleavage, chemical vapor deposition (CVD) techniques, thermal treatment of multilayered carbon nanotubes, or layer-by-layer growth.

In this Letter, we report on an alternative route to obtain MLG using nanomechanical folding induced by an AFM tip. The movement of the probe tip is controlled in order to initially cut a SLG and then fold it to form MLG. Interestingly, the folding is created at the heart of the layer and independently from the edges. The interlayer interaction in this folded graphene is expected to differ substantially from that derived from the previously mentioned fabrication methods for MLG. Indeed, Raman microscopy analysis, performed to characterize the properties of these MLGs, evidences that this folded graphene behaves as weakly interacting MLGs (wi-MLGs), without doping or strain, and emphasizes the role of the structural defects caused by the folding process.

Raman Spectroscopy Background. Mainly due to the double resonance (DR) mechanism, which is based on electron scattering by incoming light that selects phonons that satisfy wavevector and energy conservation close to K and K' points of the BZ, resonance Raman microscopy of graphenic materials is a key characterization technique. It can give information on structural, mechanical, and electronic properties. A typical Raman spectrum of graphene is dominated by two or three intense bands plus less intense combination bands. The in-plane vibration G band, with E_g symmetry at the Γ point of the BZ, lies at 1582 cm⁻¹; the defect-induced D band, with A_g symmetry, lies close to 1350 cm⁻¹ using a laser wavelength of λ = 514 nm, and the two-phonon DR 2D band lies close to 2680 cm⁻¹ with λ = 514 nm, both close to the K points. Whereas the D band is activated by defects in the crystal structure, the 2D band, involving the scattering by two phonons, is always present in the spectrum. Due to both the DR mechanism and the phonon dispersion, the D and 2D band positions depend on the laser wavelength used. The 2D band shape is found to be Lorentzian for supported graphene but is asymmetric for free-standing graphene, being the inner process, the DR mechanism selects phonons that have slightly different energies, leading to the two contributions forming the asymmetric profile. The subband at the lowest wavenumber (2D₁) is attributed to the inner process, whereas the band at the highest wavenumber (2D₂) is attributed to the outer process. A level of doping higher than 2 × 10¹¹ cm⁻², due to interaction with the substrate or using an electrostatic field, destroys this bimodal shape. A lower value of doping is found to modify the distance between the 2D₁ and 2D₂ bands. The intensity ratio of these bands has been found to be close to ~3.5 with λ = 514 or 633 nm and a frequency difference in the range of 6.6–12 cm⁻¹. Higher doping can affect also other parts of the Raman spectrum: position and width of the G band (ω_G and Γ_G, respectively) and relative intensity ratio I_D/Γ_G. Mechanically strain can also affect the Raman spectrum. The 2D band position plotted as a function of the G band position (labeled as G(1) vs G(2) plot) has been found to be able to disentangle electron or hole doping from macroscopic strain effects (for doping higher than ~10¹² cm⁻²). A slope close to 2 in that plot reveals a pure macroscopic strain effect, a slope close to 0.7 reveals pure doping, and intermediate values reveal a combination of the two effects that can be disentangled using basic algebra.

Depending on the density of in-plane defects or on the doping level, band widths and intensity ratios of D and 2D bands over G band are also used to better characterize material properties. For example, in the case of graphite, I_D/I_G has been frequently used to quantify the aromaticity, i.e., the in-plane crystalline quality: the higher the I_D/I_G, the smaller the aromatic domain size (L_G). The shape of the 2D band of graphitic materials contains information on the stacking, as reported early. For bilayer graphene (BLG), the shape of the 2D band (with a width close to 50 cm⁻¹ or higher) is more complex: it is split in four subbands that are related to scattering processes involving also interaction of the π and π* orbitals of the two sublayers. Introducing a stacking defect in BLG can change drastically its properties as well as the 2D band shape. Concerning the G band intensity, an increase up to x60 very sensitive to both L_G and the twisting angle is reported to be due to sublayer interaction. For MLG, the 2D band, giving access to electronic structure information through the DR mechanism, allows one to retrieve information from the way graphene sheets are connected. The 2D band shape changes from a quasi-Lorentzian or bi-Lorentzian shape for a SLG to a composition of several bands for MLG (at least four bands for BLG). However, for not well-stacked MLG, it has been shown that the profile is close to that of a SLG because stacking a SLG on a SLG does not necessarily lead to the properties of a BLG. Moreover, a folded SLG on top of a SLG leads to two separated SLGs but with a lower Fermi velocity. Compared to SLG, the 2D band blue shifts (in the range of 4–12 cm⁻¹), whereas the G band shifts by less than 1 cm⁻¹. Similar results have been found for misoriented MLG (up to 6 layers) that lead to Lorentzian profiles and blue shifts of the 2D band. Finally, we mention the weak asymmetric combination band D + D* at 2450 cm⁻¹, which originated by the inner scattering process plus phonons coming from the ΓK high-symmetry line of the BZ, whose shape and position depend on the number of stacked layers.

Experimental Procedures and Raman Analysis. SLG samples have been obtained from CVD graphene deposited onto Cu and transferred by means of PMMA spin coating on a Si wafer (with a Si native oxide layer of a few nm). Acetone was used to remove the PMMA. In order to obtain the best SLG, labeled as pristine hereafter, we tested different experimental conditions varying CH₄ and H₂ flows, the baking time during spin coating, the nature of the etchant, and the time acetone was applied to remove PMMA (see the Supporting Information for more details). Measurements were performed in air. Raman spectra were obtained using a Horiba Jobin Yvon HR800 setup with an excitation wavelength of λ = 514 nm, a ×100 objective (numerical aperture of 0.9, i.e., a theoretical spot radius of 0.34 μm), a 600 grooves/mm grating, and 5 mW power. The resolution was about 1 cm⁻¹. We selected a sample with the following Raman features: I_D/I_G = 2.3, ω_G = 2678 cm⁻¹, I_G = 1581 cm⁻¹, I_G = 37 cm⁻¹ (falling in the range admitted for SLG 2D band), and I_G = 25 cm⁻¹. Raman maps were
performed with a lateral displacement step of 250 nm, and data were extracted from these maps. In specific cases, to increase the signal-to-noise ratio, spectra were averaged from several relevant $\mu$m$^2$ zones, after checking that they were homogeneous.

To cut and modify the pristine SLG, we used an atomic force microscope (AFM) tip, as introduced in refs 46 and 47. Starting at the bottom left of a 4 $\times$ 4 $\mu$m$^2$ square and finishing at the top right, the tip scanned the square with zigzag movements in 512 lines of 4 $\mu$m (with an overlapping of the contact zone from one passage of the tip to the other as the tip radius is $\sim$10 nm) at a speed of 8 $\mu$m s$^{-1}$. The vertical force applied was set constant for a given square, and several forces, ranging from 0.2 to 11.1 $\mu$N, were tested on 25 separate squares. For a square, the first passage is supposed to cut the SLG on a 4 $\mu$m length, whereas the subsequent zigzag movements have two roles. First, they constantly apply a strain in the horizontal plane, pushing and folding graphene. Second, they help in cutting graphene from the edges perpendicular to the direction of the first passage. The AFM used in a tapping mode is an Agilent 5500 microscope, used in liquid medium (acetonitrile + hydrogen peroxide). The tip is a commercial silicon tip (AppNano ACT type, cantilever length 125 $\mu$m, nominal frequency 300 kHz) coated with the 1,4,7-triazacyclononane ligated manganese complex, as explained in refs 46 and 47. Note that investigating the role of the coating and its related chemical influence is beyond the scope of this Letter.

First Raman Analysis: Evidence for the Formation of a Weakly Interacting MLG. Graphene is cut for forces equal to or higher than 1.5 $\mu$N. For these forces, graphene is pushed on the top and on the sides of the scanned square, as can be seen in the image obtained by AFM, Figure 1a. Graphene pushed on top appears as a rectangular band with dimensions of $\sim$300–600 nm wide and 4 $\mu$m long, as measured from raw images, covering a projected surface area of 2.4 $\pm$ 0.2 $\mu$m$^2$. Graphene pushed on sides appears as small isolated patches. Figure 1b displays a typical line profile showing that the apparent height is about 30–45 nm on average, with peaks locally reaching up to 75 nm high. Figure 1c displays a typical Raman spectrum of graphene.
pushed graphene in comparison with a typical one of pristine graphene (outside of the scanned zones). The main bands of the pushed graphene spectrum are the G and 2D bands, with a G bandwidth similar to that of the pristine SLG, showing that the main graphene properties remain during the process. A small D band appears, which shows that some defects are introduced (as discussed below). The 2D band position is shifted from 2678 cm$^{-1}$ for the pristine graphene to $\sim$2700 cm$^{-1}$ for the pushed one, with a shape that is a bimodal Lorentzian profile. Figure 1d shows a full map of the studied graphene area, the scanned zones being indicated by the white dotted squares. The first, second and third squares are not commented in this study as the tip force was not enough to remove graphene. In this map, the relative intensity of the G band is displayed for each force (from 0.2 to 11.1 $\mu$N) on a logarithmic scale. The surrounding areas (in light blue) have a relative intensity of $I_G/I_{G\text{ pristine}} = 1$ (arbitrary units, 0 in log scale) and correspond to pristine graphene. The scanned zones (in dark blue) have intensities at the noise level, meaning that graphene was completely removed by the tip movement. The top zones (in yellow and red) display the highest G band intensities, with a multiplication factor when compared to pristine graphene up to $I_G/I_{G\text{ pristine}} \approx 100$ (arbitrary units, 2 in log scale), while the side zones (in cyan) have a moderate multiplication ($I_G/I_{G\text{ pristine}} \approx 3$).

The 2D band (Figure 1) behaves neither like bi-, tri-, or quadrilayer graphene nor like graphite$^{29,30,31}$ but behaves like SLG, with a single or a bimodal Lorentzian shape, which is an indication of a stacking misorientation and then of a weaker interaction between planes. Compared to SLG, its position is blue-shifted by 10–20 cm$^{-1}$, which may be due to a reduction of the Fermi velocity.$^3$ Figure 1f displays the weak D + D$^*$ band, which also compares better with SLG, although with a larger width, than with bi-, tri-, or quadrilayer graphene. Because both the laser spot and the folded zone are hundreds of nanometers large, it could be reasonable to think that all of the main graphene properties remain during the process. A combination of different geometries could be found inside of the folded graphene band, with different numbers of layers and different interlayer spacing. Figure 1g showing that a large range of geometries could give similar significant intensity enhancements, even if it is very improbable that 80 layers are present. Note that, according to the calculations, introducing small random variations of the interlayer distance could also modify intensities, up to a maximum of $\pm 30\%$ (not shown).

Other factors can also affect the intensity of the G band, which will be discussed in the last part of this paper. In the next part, we will discuss structural, electronic, and mechanical properties of this MLG with the help of the relations between the 2D and G band features by plotting $\omega_{2D}$ vs $\omega_G$ and $\Gamma_{2D}$ vs $\Gamma_G$.

To check the presence of doping or strain, we display a $\omega_{2D}$ vs $\omega_G$ plot in Figure 2a, where the two straight lines corresponding to the effect of electron and hole doping$^{31,32}$

![Figure 2](image-url)  
**Figure 2.** (a) Doping and strain characterization with a $\omega_{2D}$ vs $\omega_G$ plot. Data from Bayle et al.$^{28}$ have been $\omega_G$ corrected using a 2D band dispersion of 100 cm$^{-1}$/eV. Straight lines correspond to the behavior under doping (blue) or strain (violet).$^{33−37}$ (b) Structural characterization with a $\Gamma_{2D}$ vs $\Gamma_G$ plot.
Figure 3. Raman profiles of top pushed graphene zones. (a) $I_D/I_G$ profiles for tip forces of 1.5, 4.2, and 8.1 μN. (b) $I_D/I_G$ profile for tip forces of 9.4, 10.3, and 11.1 μN. (c,d) Same as (a) and (b) for $\Gamma_\text{G}$ profiles. Gray boxes emphasize the zone centers. The inset in Figure 3d represents $A_\text{G}/A_\text{G} \times E_\text{G}^{\text{L}}$ as a function of $\Gamma_\text{G}$. The dotted line is from ref 39, with $I_D = 500$ nm (see text).

and to the effect of strain. These $\omega_{2D}$ vs $\omega_{2G}$ plots are sensitive to doping larger than $\sim 1 \times 10^{12}$ cm$^{-2}$ and strain larger than $\sim 4\%$.

Consistently, the pristine graphene data point is close to the intersection of these two lines, which corresponds to suspended graphene (no doping and no strain). The w/MLG folded graphene data points of this work follow neither of these lines. They draw roughly a vertical line: $\omega_{2D}$ is nearly constant in the range of 1579–1581 cm$^{-1}$, while $\omega_{2G}$ is in the range 2677–2702 cm$^{-2}$. Values obtained for the side pushed graphene are smaller than those for the top pushed graphene, the maximum blue shift compared to pristine graphene being $\sim 25$ cm$^{-1}$. Similar blue shifts have been observed previously for not well stacked graphene layers and attributed to a reduction of the Fermi velocity. We then conclude here that pushed graphene has a lower Fermi velocity than pristine graphene (about 0–6% less for side pushed graphene and about 5–11% less for top pushed graphene), whereas neither doping nor strain effects are observed within Raman sensitivity.

$I_{2D}/I_G$ was found to vary from $\sim 0.4$ to 3 without distinction between top and side pushed graphene. As electromagnetic interference due to multiple reflections accounts for only as much as 30% in the $I_{2D}/I_G$ ratio variation, there is another origin for this ratio variation. These calculations are detailed as Supporting Information. $\Gamma_{2D}$ was found in the range of 35–58 cm$^{-1}$, centered at about 40 (50) cm$^{-1}$ for top (side) pushed graphene, in the same range as what was observed for misoriented stacked MLG in ref 28. Data points are displayed in a $\Gamma_{2G}$ vs $\Gamma_{2D}$ plot in Figure 2b. The side pushed graphene data points are gathered around $\Gamma_{2G} = 25$ cm$^{-1}$ (in the range of 18–26 cm$^{-1}$), and the top pushed graphene data points are gathered around $\Gamma_{2D} = 20$ cm$^{-1}$ (in the range of 18–22 cm$^{-1}$), presenting a shift in $\Gamma_{2G}$ of 4–12 cm$^{-1}$ from the pristine graphene data point. They are compared to graphitization trajectories obtained with carbonaceous materials such as anthracene, pitch and saccharose cokes, fibers, and pyrocar-
Data are gathered in the low part of both the energy used) as a function of
that mainly sensitive to $E_L$ and $E_G$. These two types of defects can be
associated with two lengths (1-d), such as crystallites borders or dislocations.

$\mu N$ zones will be referred to as low defect zones.

observed that both $L_D/I_C$ and $\Gamma_G$ values are larger for the three
smallest tip forces (Figure 3a,c) than those for the three largest
(Figure 3b,d). This indicates that at the zone centers more
defects are accumulated than the lowest forces. Considering that
the zone edges can be significantly more affected by the cut and
push process than the zone centers, we will focus in what
follows on the zone center properties; the 1.5, 4.2, and 8.1 $\mu N$ zones
will be referred to as high defect zones, while the 9.4, 10.3, and 11.1 $\mu N$ zones will be referred to as low defect zones.

The origin of these defects is not obvious. They can be zero-
dimensional (0-d), such as dopant or vacancies, or one-
dimensional (1-d), such as crystallites borders or dislocations.

These two types of defects can be associated with two lengths
$L_D$ and $L_u$ respectively. To retrieve $L_D$ and $L_u$ values, we use
Figure 2b of ref 39 and plot $A_D/A_C \times E^4_f$ ($E_f$ being the laser
energy used) as a function of $\Gamma_G$ (inset of Figure 3d). Note that
$A$ refers to the band integrated area, while $I$ refers to the band
height. Here, $A_D/A_C$ approximately equals $2.2 \times L_D/I_C$.

We now consider the analysis of the inner and outer
scattering processes that compete in the shape of the 2D band
by fitting it with a single or a bimodal Lorentzian (Figure 4).
For $\mu N$ (high defect zones), whereas spectra 5–6 (7–8) are typical of the edges of the pushed
graphene, respectively. Spectra 3–4 are typical of the edges of the pushed
graphene zones created with a tip force higher than 9 $\mu N$ (low defect zones). In all cases, the
2D band residue is lower for the bimodal than for the
single Lorentzian fit, which confirms the quality of the
individual graphene layers and the weakness of the interlayer
interaction, as discussed above.

A $2D_-$ band ($\Gamma_{2D_-} \approx 50–55$ cm$^{-1}$) significantly broader
than the $2D_+$ band ($\Gamma_{2D_+} \approx 30–40$ cm$^{-1}$) is found for spectra
3–4, whereas $2D_-$ and $2D_+$ band widths are similar ($\Gamma_{2D_-}$ and
$\Gamma_{2D_+} \approx 30–35$ cm$^{-1}$) for spectra 7–8. The evolution of both
$\Gamma_{2D_-}$ and $\Gamma_{2D_+}$ along the profile of each pushed graphene zone

Figure 4. 2D$_{-}$ and 2D$_{+}$ sub-bands of graphene pushed on top. (a) Fits with one (top) or two (bottom) Lorentzians for (1–2) pristine graphene,
(3–4) the edge of the 8.1 $\mu N$ zone, and (5–6) the edge and (7–8) the center of the 11 $\mu N$ zone. (b) 2D$_{-}$ (full square) and 2D$_{+}$ (empty circle)
width profiles for tip forces of 1.5, 4.2, 8.1, 9.4, 10.3, and 11.1 $\mu N$. (c) $\mu N$ vs $\Gamma_{2D}$ plot for the same tip forces, restricted to data at the zone
centers (gray areas in Figure 3). (d) $A_D/A_C$ vs $A_{2D_-}/A_{2D_+}$ plot with data from Figure 4c restricted to the conditions $\Delta \Gamma_{2D} < 10$ cm$^{-1}$ and $\Gamma_G < 19$
cm$^{-1}$. Dotted lines are guides for the eyes. Pristine SLG lies accidentally in the high defect line, as justified in the text.
is displayed in Figure 4b. Except for the highest force (11.3 μN), the 2D+ bandwidth values are larger and more spread than those for the 2D band. For applied forces higher than 9 μN, Γ_{2D+} tends to equal Γ_{2D−} at the center of the profile. For lower forces, equality is not reached, but the difference between the two widths is minimum close to the center. These trends suggest that the 2D+ and 2D− bandwidths are sensitive to defects (the lesser the number of defects, the closer the widths), the 2D− bandwidth being more sensitive than the 2D+ band. Figure 4c displays ω_{2D+} and ω_{2D−} as a function of Γ_{2D+} and Γ_{2D−}, for the sampling points located at the zone centers (gray boxes in Figure 3). Remarkably, all of the 2D+ data points are gathered in the ω_{2D+} range from 2696 to 2708 cm\(^{-1}\) and the Γ_{2D+} range from 24 to 40 cm\(^{-1}\), while the 2D− data points are separated around two branches having the same slope. The upper branch contains 2D− data points from the high defect zones (tip forces below 9 μN), while the lower branch contains most of the 2D− data points from the low defect zones (tip forces above 9 μN, some points from the zone at 10.3 μN lying in between the two branches). These results confirm that the 2D− band characteristics are sensitive to structural defects and that the 2D+ band is more sensitive than the 2D− band. Branch 2 is downshifted horizontally by ΔΓ ≈ 12 cm\(^{-1}\) and vertically by Δω ≈ 15 cm\(^{-1}\). It has been shown in ref 31 that Γ_{2D+} and Γ_{2D−} depend on v\(\_\text{Dirac}\) and v\(\_\text{Dirac}\) for where γ\(\_\text{Dirac}\) is the broadening of the electron state involved in the inner (outer) scattering processes, composed of several contributions (electron–electron, electron–phonon, and defect), and v\(\_\text{Dirac}\) (v\(\_\text{Dirac}\)) is the Fermi velocity of the corresponding electronic band. Our results indicate that v\(\_\text{Dirac}\) γ\(\_\text{Dirac}\) or most probably both of them depends on the graphene structural defects. The reduction of the Fermi velocity, previously discussed with Figure 2a, could explain here the vertical upshift (increase of the 2D− band position) from the low to the high defect branch. Moreover, increasing the amount of defects is expected to increase γ\(\_\text{Dirac}\) and this could explain the existence of the two branches, depending on the defect amount. Moreover, a significant G band intensity enhancement is observed when simultaneously Γ_{2D+} is close to Γ_{2D−}, and Γ_{G} is not too large (<19 cm\(^{-1}\)). Pure graphene corresponds to a ratio A_{2D}/A_{G} higher than 6, and the G band enhancement, which corresponds to low A_{2D}/A_{G} values, has been attributed to a change of the quantum interferences involved in the G band intensity calculation appearing when doping.\(^{53,56-58}\) Here, a similar process likely exists as the two conditions diminish the value of γ\(\_\text{Dirac}\) that appears in the denominator of the G band Raman cross section and thus increases the intensity,\(^{57}\) but structural defects and not doping are at the origin of the interference changes. Figure 4d plots the intensity ratio A_{2D}/A_{3D}, as a function of A_{2D}/A_{G} obtained for samples obeying the two conditions: ΔΓ_{2D} < 10 cm\(^{-1}\) and Γ_{G} < 19 cm\(^{-1}\). A_{2D}/A_{G} values range from 0.5 to 6, emphasizing A_{G} changes, A_{2D} being roughly constant. Two straight lines are obtained, one drawn mainly by high defect zones and the other one drawn mainly by low defect zones. Pristine graphene lies in the continuity of one of the lines, but it is known that the A_{2D}/A_{G} for pristine graphene can vary by up to 600% when ripples are suppressed,\(^{59}\) suggesting that the alignment with the high defect line and pristine graphene is accidental. This plot strongly suggests first that there is a correlation between inner and outer process changes and the G band quantum interference changes and, second, that these changes are induced by structural defects. The decrease of A_{2D}/A_{3D}, when A_{G} increases indicates that, while inner processes are dominant for SLG (2D− dominant), structural defects make outer processes prevail. These results echo the recent work of ref 60, who studied graphene on Cu and Cu_{3}O and observed a 2D band blue shift that can be attributed to neither strain nor doping effects and that has been related to outer processes, highlighting the need for new theoretical calculations to understand experiments.

We report on the formation of undoped weakly interacting MLG (wi-MLG) by using nanomechanical folding induced by an AFM tip on CVD-transferred graphene. Vertical forces in the μN range were applied on 4 μm square zones that induced a cut and push process leading to the formation of wi-MLG. We obtained a large set of data to characterize this wi-MLG using Raman microscopy that allowed us to play with the amount of structural defects. The spectroscopic analysis indicates that this wi-MLG behaves neither as graphite nor as well-stacked graphene but, interchangeably, as graphene sheets in weak interaction, the in-plane graphene quality being maintained after folding, with large aromatic domains limited by the edges of the folded sheets. The 2D band was found to be composed of the two subbands 2D+ and 2D− originating in the so-called inner and outer processes involved close to the Dirac cones and blue-shifted up to 20 cm\(^{-1}\), suggesting a Fermi velocity reduction. Although the 2D band exists independently of structural defects involving two phonons in the DR mechanism, its shape was found here to depend on them, the 2D− band being much more dependent than the 2D+ band. For the samples containing the lowest amount of structural defects, the 2D+ band intensity was found to be larger than that of the 2D− band, and a correlation with changes in the G band intensity was observed. These results suggest that inner and outer processes and G band quantum interferences are related and that they are most probably both related to the amount or the nature of structural defects. This point needs to be confirmed by additional and complementary experiments and future theoretical efforts. This work could complete the recent field of graphene origami/kirigami consisting of controlling the 3-d shape to manipulate electronic and material properties and help in better characterizing 3-d graphene involved in many applications.

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■ LIST OF ABBREVIATIONS

$\alpha_X$ (expressed in cm$^{-1}$): band position of the band labeled X (X could be G, 2D, D', etc.); $I_X$ (expressed in cm$^{-1}$): full width at half-maximum of the band labeled X; $A_X$ (expressed in arbitrary units related to the number of counts on the detector): height of the band labeled X.; $E_F$ energy (expressed in eV) of the laser used for Raman analyses.; SLG: single-layer graphene; BLG: bilayer graphene; MLG: multilayer graphene; AFM: atomic force microscope

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