Mass-related inversion symmetry breaking and phonon self-energy renormalization in isotopically labeled AB-stacked bilayer graphene

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A mass-related symmetry breaking in isotopically labeled bilayer graphene (2LG) was investigated during in-situ electrochemical charging of AB stacked (AB-2LG) and turbostratic (t-2LG) layers. The overlap of the two approaches, isotopic labeling and electronic doping, is powerful tool and allows to tailor, independently and distinctly, the thermal-related and transport-related phenomena in materials, since one can impose different symmetries for electrons and phonons in these systems. Variations in the system’s phonon self-energy renormalizations due to the charge distribution and doping changes could be analyzed separately for each individual layer. Symmetry arguments together with first-order Raman spectra show that the single layer graphene (1LG), which is directly contacted to the electrode, has a higher concentration of charge carriers than the second graphene layer, which is not contacted by the electrode. These different charge distributions are reflected and demonstrated by different phonon self-energy renormalizations of the G modes for AB-2LG and for t-2LG.

Graphene, which is a gapless material, has gathered much attention due to its prospective fascinating applications. However, some of the proposed applications, such as transistor-based applications, cannot be realized in single layer graphene due to fundamental problems related to, for example, a creation of a band-gap. As an alternative, bilayer graphene (2LG) with AB stacked layers (AB-2LG) has different vibrational properties and also a different electronic structure than monolayer graphene (1LG) and might overcome some of the shortcomings of 1LG. For example, in AB-2LG it is possible to tune a bandgap by an external electric field, which enables realization of a field effect transistor with a tunable bandgap1,2. These potential advantages motivated several recent studies involving AB graphene1,3–7.

Another challenge is the difficulty to address and probe individual layers in few layer graphene samples. This problem can be promptly solved by isotopic labeling of individual layers, as has been recently demonstrated8,9. One can easily tune the frequency of the phonons by an exchange of the 12C isotope with a 13C isotope with essentially no change to the electronic structure. In this context, while isotopic labeling tunes the phonon properties (tuning, therefore, a gas of Bosons in the system), electronic doping provides an important tool to tune the electronic properties of graphene (tuning, therefore, a gas of Fermions in the system)10–12. It is important to note that, this approach tunes, distinctly and independently, the electronic and vibrational properties of the material. Indeed, by varying the ways one isotopic labels and/or electronic dopes the system, different symmetries can be achieved to describe phonons and electrons in the system, which allow us to control selection rules often important to describe several physics-related phenomena. As a consequence, we gain a powerful method to tailor the thermal-related and transport-related phenomena in the material.

The changes in the vibrational structure can be observed directly by Raman spectroscopy. The larger the amount of 13C isotope that is introduced into the graphene layer, the lower the observed frequency of the Raman bands8,9. If the different layers in a few layer graphene sample contains different amount of 13C isotope, one can distinguish their Raman bands in the isotopically doped spectra relative to that for the corresponding naturally occurring graphene layer containing only 12C8,9. Also, the electronic doping can be realized by electrostatic
gating, electrochemical charging or chemical doping and several reports on charge-induced phenomena in 1LG are found in the literature for each of these doping methods. In few layer graphene (FLG) samples, the situation is more complex. Although the doping of 2LG and FLG has been reported, the results are difficult to interpret, since it is not clear how the doping charge is distributed between the various graphene layers. This problem can be overcome by the sequential transfer of 12C and 13C graphene layers onto, for turbostratic 2LG (t-2LG), since a special 2LG sample can be interpreted, since it is not clear how the doping charge is distributed in these samples one can determine the doping charge associated with each individual layer independently when both layers were similarly doped, as reported in Ref. 8. The experimental results from Ref. 8 suggested that the charge is distributed almost evenly between the top and bottom layers of 2LG when the two constitutent layers are randomly stacked on a SiO₂ substrate.

As discussed above, the turbostratic FLG can be easily obtained by the subsequent deposition of 12C and 13C individual layers on the target substrate. However, this procedure does not allow one to control the rotation angle between the graphene layers, and for this reason, it is not possible in this way to obtain AB-2LG. Recently, several studies of graphene add-layers (as grown in CVD methods) appeared. These add-layers are additional graphene layers formed during the growth of a primary 1LG using a Cu catalyst and in many cases, AB stacked regions are observed for the add-layer relative to the continuous graphene layer. It has been shown that, even though the add-layers grow much slower than the primary 1LG, they continue to grow over the entire growth time. Therefore, one can, by careful control of the isotopic content of the CH₄ source and the reaction conditions, reach the situation where the top add-layer contains mostly one type of isotope (either 12C or 13C), while the continuous layer comprises the second type of isotope.

In the present study, we tuned the chemical vapor deposition (CVD) synthesis of the graphene bilayer to form AB stacked regions where the add-layer is synthesized from 13C and the continuous layer (primary 1LG) is synthesized from 12C isotope, as shown in Fig. 1. In such a sample, we are able to address individual layers by Raman spectroscopy, follow the effect of phonon self-energy renormalizations for each individual layer separately and further understand how the interlayer (IL) interactions work in these isotopic systems.

**Results**

**Raman spectra for the 12C/13C 2LG systems.** The graphene samples were grown on a copper substrate and transferred to a SiO₂/Si substrate following the procedure in Ref. 21. During the growth, we changed the carbon isotope as follows: at the beginning of the growth we introduced 12CH₄ for 90 s. Next, we changed the carbon source to 13CH₄ and we continued the growth for 5 minutes more. Since the growth of the continuous layer is fast and the growth of the add-layer is slow, we obtained 2LG regions where a small central area is composed only from the 12C isotope and the border area (about 70% of the sample) is composed of the 13C isotope. The continuous layer that formed first is composed of the 12C isotope. Figure 1(a) shows a photograph of the resulting graphene sample obtained using an optical microscope after transfer of the so-called 2LG thus prepared onto a SiO₂/Si substrate. The hexagonal shaped darker region (delimited by the black dotted line) in Fig. 1(a) corresponds to the 2LG, while the rest of the area (the background area) of the imaged spot is covered by 1LG. Raman Figure 1(b) shows a 2D Raman map plotting the G’(2D) spectral linewidth. The G’(2D) lineshape is very sensitive to the 2LG stacking order as well as to the isotopic composition of the layers. In Fig. 1(b) it is possible to localize the 12C 1LG, the 12/13C AB-2LG as well as the 12/13C AB-2LG.

Figure 2 shows a typical Raman spectrum of the 2LG inner region thus prepared in comparison to that of the 12C 1LG outer region (note that the 13C sample is expected to contain the natural isotopic abundance, which is 1.07% of 12C). Figure 2 also shows the Raman spectrum for a standard CVD-derived 12C 1LG. As expected for isotopic systems, the Raman spectrum of the 13C 1LG sample exhibits the same Raman features as the Raman spectrum of the 12C 1LG except for a downshift of all the Raman bands for the 13C 1LG sample relative to those of the 12C graphene sample. The observed experimental downshifts of the D, G and the G’ bands for the 13C graphene with respect to those of the 12C graphene are about 50 cm⁻¹, 60 cm⁻¹ and 100 cm⁻¹, respectively². In a continuum model, the frequency shifts of the Raman bands in the 13C enriched material with respect to the 12C counterpart originate from the increased mass of this isotope which is given by equation (1):

\[
\frac{(\omega_0 - \omega)}{\omega_0} = 1 - \left(\frac{12 + c_0}{12 + c}\right)^{1/2}
\]

where \(\omega_0\) is the frequency of a particular Raman mode in the 12C sample, \(c = 0.99\) is the concentration of 13C in the enriched sample,
and $c_0 = 0.0107$ is the natural abundance of $^{13}$C in a typical $^{12}$C sample. According to equation (1), the downshifts of the D, the G and the G' bands are expected to be 48 cm$^{-1}$, 56 cm$^{-1}$ and 95 cm$^{-1}$, respectively, which is in good agreement with our previous experimental results.

In the present work, we analyze the areas of the 2LG sample which comprise the initial $^{12}$C 1LG and the $^{13}$C regions of the add-layer composing this layered graphene ($^{12/13}$C 2LG). As expected (see Fig. 2), we observe two G modes in the Raman spectrum, one arising from the $^{12}$C layer and the second arising from the $^{13}$C layer. The as-grown peak positions of these G bands are at 1587 cm$^{-1}$ and 1530 cm$^{-1}$, respectively. Interestingly, in the case of the G' Raman mode, we obtained only a broad asymmetric band. This is in contrast to the situation in t-2LG prepared by the subsequent transfer of two mode, we obtained only a broad asymmetric band. This is in contrast of the $^{12/13}$C AB-2LG we obtain 4 peaks due to the fact that iTO region. For the $^{12}$C G mode is not, and therefore only one peak is seen in the G band top and bottom layers. Note that, while the S mode is Raman active, optical (LO) and the in-plane tangential optical (iTO) modes of the asymmetric (AS) mode would double giving eight Raman bands. The frequencies of each of these eight bands are close to each other, and therefore only one asymmetric broad band is observed experimentally in the Raman spectrum (Figure 2). It is worth mentioning that, due to its particular mechanism, this somewhat asymmetric G' mode lineshape is a spectroscopic signature for the $^{12/13}$C AB-2LG systems.

For the $^{12/13}$C AB-2LG the situation is slightly different. Likewise the case of $^{12/12}$C AB-2LG, the unit cell of a $^{12/13}$C AB-2LG is composed of 4 atoms but now the atoms of the top layer are $^{12}$C atoms while the atoms in the bottom layer are $^{13}$C atoms. This has a very important symmetry consequence: because the $^{13}$C and $^{12}$C atoms have different masses, the unit cell for the $^{12/13}$C AB-2LG system has no inversion symmetry anymore for the phonons (note that for electrons the symmetry is kept) like is observed for the $^{12/12}$C AB-2LG system. Therefore, we have a mass-related symmetry breaking and the main consequence is that those S and AS modes discussed for $^{12/12}$C AB-2LG are no longer eigenstates of the system. Instead, the new eigenstates are now a mixing of the S and AS modes and the G mode region must comprise two Raman active peaks. A very similar effect happens when one applies an electric field in a $^{12/13}$C AB-2LG system. However, in this case the inversion symmetry is broken for both electrons and phonons, so that we have a band gap opening in the K-point and, the S and AS modes are mixed and the G mode region has two Raman active peaks. Regarding the S and AS iTO phonon resonances, they are no longer unique around K(K'-point), as is the case for the $^{12/12}$C AB-2LG. Due to the mass-related symmetry breaking, we now have two pairs of S and AS iTO mode resonances and the total number of bands contributing to the G' mode would double giving eight Raman bands. The frequencies of each of these eight bands are close to each other, and therefore only one asymmetric broad band is observed experimentally in the Raman spectrum (Figure 2). It is worth mentioning that, due to its particular mechanism, this somewhat asymmetric G' mode lineshape is a spectroscopic signature for the $^{12/13}$C AB-2LG systems.

**Gate-modulated Raman spectroelectrochemistry.** Next, we discuss the Raman spectroelectrochemistry results for the $^{12/12}$C AB-2LG systems. Figure 3 gives a schematic illustration of the experimental setup used here in which only the $^{12}$C layer is connected to the electrode. Figure 4(b) shows the Raman spectra of $^{12/12}$C AB-2LG at different electrode potentials separated by 0.1 V. Interestingly, the behavior of the Raman spectra for $^{12/12}$C AB-2LG (Fig. 4(b)) is strongly different from that of $^{12/13}$C t-2LG (Fig. 4(a)). From now on, the following convention will be adopted: the Raman features in Figs. 4(a) and (b) both present two G modes; one with higher frequency, which is going to be called the HG mode and one with lower frequency, which is going to be called the LG mode. At first glance, especially in the positive potential regimes, one may identify some similarity between the potential dependent behavior of the HG modes for the $^{12/12}$C AB-2LG and t-2LG systems. However, the behavior of the LG mode for the $^{12/13}$C AB-2LG is completely
different from both G mode lineshapes, that is, different from both the HG and LG modes of the 12/13C t-2LG. Namely, for the LG mode of the 12/13C AB-2LG, we observe small changes in the G mode frequency during negative doping. The LG mode downshifts from 1535 cm\(^{-1}\) to 1528 cm\(^{-1}\) going from 0 to -1.5 V. The corresponding frequency change in the LG mode of the 12/13C t-2LG (Fig. 4(a)) is much larger, and has an opposite direction: from 1528 cm\(^{-1}\) to 1546 cm\(^{-1}\). For positive electrochemical potentials, we observe a larger change from 1535 cm\(^{-1}\) (at 0 V) to 1546 cm\(^{-1}\) (at 1.5 V) for the LG mode in AB-2LG, as seen in Fig. 4(b), but this frequency change is still smaller than in the case of the LG mode in t-2LG for which the change is from 1528 cm\(^{-1}\) (at 0 V) to 1563 cm\(^{-1}\) (at 1.5 V) as shown in Fig. 4(a).

In charged graphene, the frequency shift of the G mode, which is a first-order Raman mode around the \(\Gamma\)-point whose phonon momentum is null \(q = 0\), is related to both, the change in the C-C bond strength and the renormalization of the phonon self-energy associated with many-body effects\(^{17}\). Since for graphene a coupling between the lattice vibrations and the Dirac fermions is allowed (because the energy scales for the electron and phonon dynamics are comparable) the adiabatic Born-Oppenheimer approximation fails to describe phonons in graphene\(^{14}\). As a consequence, the interaction of the carriers in graphene with phonons must be included. These interactions cause electron-hole (e–h) pair creation (annihilation) due to phonon absorption (emission), with a lifetime related to the phonon linewidth (\(\Gamma\)), as observed in the Raman spectrum. This leads to a renormalization of the phonon energy, the phonon lifetime and consequently the energy of the carriers, that is, for both electrons and holes\(^{22,23}\). In charged graphene, every time we have a real creation (annihilation) of e–h pairs, which means that the phonon energy \(E_{\text{ph}}\) is bigger than \(2|E_F|\) (\(E_F\) is the Fermi energy), a decrease of the G mode phonon frequency occurs. When \(E_F\) is moved away from the Dirac point, the formation of e–h pairs is eventually suppressed by the Pauli principle when the phonon energy \(E_{\text{ph}}\) is smaller than \(2|E_F|\)\(^{24}\) resulting in a G mode frequency upshift for both negative and positive electrochemical potentials. It is worth mentioning that when \(E_{\text{ph}} = 2|E_F|\), the so-called Kohn anomaly takes place and the maximum softening of the G mode frequency occurs\(^{17}\).

Electrochemical doping is a reproducible and precise way to control the graphene doping, and we can easily evaluate the doping effects in graphene systems by monitoring the changes in the frequency of the Raman G mode during electrochemical charging\(^{10,11}\). To better elucidate the changes for both the LG and HG modes in the AB-2LG and t-2LG spectra, we analyzed the spectra in Figs. 4(a) and 4(b) using a Voigt line shape for (a) and (b). The fitting results are compiled in Fig. 5(b) (for both the LG and HG frequencies and linewidths of the 12/13C t-2LG) and Fig. 5(b) (for both the LG and HG frequencies and linewidths in 12/13C AB-2LG). First, we note that the frequency shifts of the LG and HG modes are observed to be smaller (for both, positive and negative potentials) for 12/13C AB-2LG with comparison to the 12/13C t-2LG. This suggests that different mechanisms are ruling the doping of 12/13C AB-2LG in comparison to the 12/13C t-2LG at the same applied electrode potential (which means the same charge concentration). Indeed, the t-2LG \(E_F\) will depend on \(n\) (\(n\) is the charge concentration) according to the following relation: | 3 : 2061 | DOI: 10.1038/srep02061 | www.nature.com/scientificreports
In order to understand the results obtained here for the LG and HG modes on potential voltage with the calculations performed in Ref. 3, we conclude that for the $^{12/13}$C AB-2LG, $n_{\text{bottom}}$ should also consider the location of the add-layer with respect to the substrate, e.g., whether the $^{12}$C layer is at the top or the bottom of the $^{13}$C continuous layer. The injection of the charge carriers is more efficient to the top layer, which is closer to the electrolyte ions than to the bottom layer which is in contact with the substrate. In our case, the add-layer is at the bottom, as commonly expected for CVD-based 2LGs. Therefore, this add-layer is electrically shielded by the top layer, and one can understand the latter observation, in which a smaller amount of charge is located on the add-layer. This is consistent with previous calculations by Das and experiments by Fang et al. We also note that a similar situation happens in the case of double wall carbon nanotubes where both outer and inner tubes are metallic and only the outer tube is contacted by the electrode. The in-situ Raman spectroelectrochemical measurements on the latter samples also demonstrated that there is more charge located on the outer tube than on inner tube.

**Discussion**

In order to understand the results obtained here for the LG and HG modes in $^{12/13}$C AB-2LG, we must, as stated earlier in the text, recall that the unit cell for this systems has 4 atoms, as is the case for $^{12/13}$C AB-2LG, with the difference that the bottom atoms of the 2LG unit cell are $^{13}$C atoms and the top atoms of the 2LG unit cell are $^{12}$C atoms. In this case, the inversion symmetry in $^{12/13}$C AB-2LG is naturally broken due to the different $^{12}$C and $^{13}$C masses. As a result, what we are observing in Figs. 2 and 4(b) is, indeed, a S and AS mixing of the $E_g$ and $E_u$ modes distinctly observed only when the inversion symmetry exists, like is the case for $^{12/12}$C AB-2LG. This mixing of the $E_g$ and $E_u$ modes has also been observed for $^{12/12}$C AB-2LG when the latter is under the effect of an electric field. Indeed, this mass-related symmetry breaking is confirmed by the electrochemistry measurements. As reported by Gava et al. a signature of the $E_g$ and $E_u$ mixing is that the intensity ratio ($I(E_u)/I(E_g)$) between the HG (an anti-symmetric combination of $E_g$ and $E_u$) and LG modes (a symmetric combination of $E_g$ and $E_u$) must increase with increasing $|E_d|$. This signature is confirmed by the experimental results, as shown in Fig. 6. Regarding the frequency, linewidth and intensity behavior of the two G band modes, Gava et al. described their dependence in terms of the net 2LG charge concentration $n = n_{\text{top}} + n_{\text{bottom}}$. According to the charge concentration for the top ($n_{\text{top}}$) and bottom ($n_{\text{bottom}}$) layers, the frequency, linewidth and intensity can assume different behaviors. Here, comparing the dependence of the HG and LG modes on potential voltage with the calculations performed in Ref. 3, we conclude that for the $^{12/13}$C AB-2LG, $n_{\text{bottom}}$ which is kept at constant potential) is positive (signifying an excess of electrons) and higher than the initial $n_{\text{top}}$. Note that to fully explain the frequency and linewidth behaviors, we still need to consider other effects such as the extinction of electron–hole (e–h) pair formation due to a band gap opening related to the application of an external electrical field and also the intraband related renormalizations of the phonon energies. Both effects will be important for the positive voltages (which means excess of holes in the system) and negative voltages (which means excess of electrons in the system). Note that, due to conventions related to electrochemistry experiments, positive voltages means that the $E_g$ is decreasing, so that holes are being injected to the system. On the other hand, negative voltages will mean that $E_g$ is increasing, so that electrons are being injected to the system. This electrochemistry convention is opposite to the convention for back-gated experiments.

Next, based on the fact that $n_{\text{bottom}} > n_{\text{top}}$, we discuss the existence of an off-set in the change of the LG and HG mode frequencies in their dependence on electrode potential, as observed for the $^{12/13}$C AB-2LG.
AB-2LG. This is, in particular, clear for the case of positive doping. As one can see from Fig. 4(b), there is a small increase in the frequency of the LG mode and almost no changes in the frequency of the HG mode up to an electrode potential of +1 V. Then, for the potentials above +1 V, the G mode frequencies are gradually increased and seem to saturate from the potential +1.3 V on. This behavior is in contrast to 1LG or t-2LG (Fig. 4a) where the frequency starts to change even at very low positive and negative applied potentials (±0.1 V). Besides the competition for the corrections in the phonon frequency between both phenomena, phonon self-energy renormalizations and changes in the chemical C-C bonds (excess of holes hardens the C-C bonds while excess of electrons softens the C-C bonds)\(^2\), in AB-2LG, one should also consider subsequent filling (emptying) of the second electronic band in the conduction band \(p_1^*\) (of the second electronic band in the valence band \(p_2\) at higher electrode potentials. This band filling (emptying) is important to decide which phenomena will dominate and rule the frequency changes. In particular, it has been shown that the filling of \(p_2^*\) may lead to a kink in the dependence of the Raman frequency on electrode potential\(^3\) and this observation is consistent with a sudden change of the slope of the frequency/potential dependence \((\Delta \omega/V)\) during hole doping (positive potentials) as seen in Fig. 4(b).\(^4\) Indeed, when \(E_F\) is at zero, real e–h pairs involving the \(p_1\) and \(p_1^*\) bands are being created all time, which contributes to decreasing the phonon frequency. At the same time, virtual e–h pairs are being created between \(p_1\) and \(p_2\) bands (in the valence band, which contributes to an increase in frequency) while no e–h pairs are being created between \(p_1^*\) and \(p_2^*\) in the conduction band. Note that, because it is a resonant effect, e–h pairs involving the \(p_1\) and \(p_1^*\) bands will dominate the virtual processes. Nothing is happening to the bonds since the system is not doped yet.

Let us now understand what happens when the system is doped with holes. In this case, when a first stage takes place (electrochemical potential between 0 and 1 V in Fig. 5(b)), the real e–h pair formation involving the bands \(p_1^*\) and \(p_1\) will be halted (since \(E_F\) is decreasing) and the e–h pairs involving the bands \(p_1\) and \(p_2\) will change their status from virtual to real e–h pairs. The net effect will be: the phonon self-energy renormalizations will decrease the frequency (broaden the linewidth), since the real e–h pair formation will favor the frequency changes, while the C-C bonds will harden hence increasing the frequency. On average, no (or a small) change in frequency is expected, in accordance with the observations. Precisely speaking, this competition between the phonon self-energy renormalizations versus C-C bond changes will certainly depend on the net charge density \(n = n_{\text{top}} + n_{\text{bottom}}\). Since this charge density will determine the \(E_F\) behavior in the system\(^4\). In our experiment, in which \(n_{\text{bottom}} > n_{\text{top}}\), the explanations given so far explain well the behavior observed for the HG mode in the \(^{12/13}\text{C}\) AB-2LG but it cannot explain completely the behavior observed for the LG mode, whose frequency slightly increases in the potential range from 0 to 1 V (see Fig. 5(b)). To completely understand the LG mode, we need to consider a band gap opening, as discussed later in the text. Going further in the electrochemical potential, in a second stage, for electrochemical potentials larger than 1 V, the 2LG system is heavily doped with holes and then both, real and virtual e–h creations (annihilations) will be halted and the C-C bonds hardening will favor the frequency changes, resulting in a steep increase of the frequency\(^4\).

When the 2LG system is doped with electrons, the virtual e–h pairs created (annihilated) due to phonon absorption (emission) involving the \(p_1\) and \(p_2\) bands will always exist, which contributes to increase the frequency. Again, in a first stage (electrochemical potential between \(-1\) V and 0), a competition between real and virtual e–h pair formations involving the \(p_1\) and \(p_1^*\) bands and the \(p_1\) and \(p_2\) bands, respectively, will occur. When \(E_F\) continues to increase, eventually the e–h pair formations involving the \(p_1\) and \(p_1^*\) bands and the \(p_1\) and \(p_2\) bands will be virtual and real e–h pairs involving the \(p_1^*\) and \(p_2^*\) bands start occurring. The net consequence is that the real electron hole pair formation together with the softening of C-C bonds will be dominating (it is worth remembering that when the graphene systems are doped with electrons, the C-C bonds soften, which results in a decrease of phonon frequencies). The net result is a decrease in the frequency, as shown in Fig. 5(b). As we progress to the second stage (electrochemical potential \(< -1\) V), all the e–h pair formations involving all the \(p_1\), \(p_2\), \(p_1^*\), \(p_2^*\) will be virtual. However, this virtual e–h pair formation will be a small perturbation favored by the C-C bonds softening. The net effect is still a decrease in the phonon frequency. It is important to comment that the behaviors observed for the phonon linewidths are consistent with our explanations.

As mentioned, the explanations above do not fully explain the behavior of the LG mode for the \(^{12/13}\text{C}\) AB-2LG in the range from 0 to 1 V, which requires a band effect to be fully understood. In fact, since the graphene is on the substrate which is known to dope graphene, we can consider this situation as a device with a fixed voltage at the bottom gate and variable voltage at the top gate, which is realized by changing the applied electrode potential. The electrochemical doping method for varying \(E_F\) has generally been shown to be very efficient for the gating of devices\(^5\). Since we gradually increase the gate voltage in our experiment, the bandgap should be opened in the \(^{12/13}\text{C}\) AB-2LG electronic structure and, in principle, the charge carriers are no longer injected into the graphene sample, until \(E_F\) exceeds the band gap magnitude. We note that in contrast to previous studies, we used a potentiostat to control the potential of the gate electrode, and therefore the electric field is expected to be higher and the gap opening can be larger than the phonon energy. The gap opening should therefore be reflected in the Raman spectra of the doped AB-2LG. The situation can be analogous to a semiconducting SWCNT, where one can find an offset in doping which is equal to half the energy of the bandgap\(^6\). At this point, it is important to remember that since one of the layers is being kept at a constant potential, the opening of a band gap is accompanied by the respective change of \(E_F\). This will make the band gap to be important at positive electrochemical voltages but unimportant for negative electrochemical voltages\(^7\). This is discussed as follows: the changes of the Raman G mode features are related to the creation (annihilation) of e–h pairs due to phonon absorption (emission) which hardens (narrows) the Raman band frequency (linewidth) and it is directly connected to the lifetime of the electron–hole pair, in other words, the average time spent by the phonon as an e–h pair. It is worth remembering that, the formation of e–h pairs can be prevented by the injection of charge carriers, to change \(E_F\) sufficiently so that energy and momentum can
no longer be conserved for e–h pair formation due to phonon absorption (emission). Indeed, we discussed that any time the condition \( E_{\text{ph}} < 2E_{\text{F}} \) (\( E_{\text{ph}} \) stands for the phonon energy) is satisfied, the formation of real e–h pairs will be halted and as a consequence the G mode frequency will increase and the respective linewidth will decrease. Alternatively, the formation of real e–h pairs can be prevented by opening a bandgap, since the real e–h pair formation will be halted every time the band gap energy (\( E_{\text{gap}} \)) is larger than \( E_{\text{ph}} < E_{\text{gap}} \). In this case, any change in frequency will be more likely related to changes in the C-C bonds since they major any contribution involving virtual e–h pair creations related to the band-gap (precisely speaking, the formation of e–h pairs involving forbidden states of the bandgap, which can be understood as a virtual e–h pair creation as well, will be unlike since these e–h pairs involve forbidden states of the system). In other words, if the \( E_{\text{ph}} > E_{\text{gap}} \) condition is satisfied, e–h pairs will be formed and the hardening (narrowing) of the G mode frequency (linewidth) should be observed independently of the \( E_{\text{gap}} \) value.

The bandgap opening, in fact, reflects spectral changes in the positive electrochemical potential values in the LG modes due to the applied gate potential, as shown in Fig. 5(b). Let us start analyzing the range of voltages from \(-1.5 \) to \(0 \) V in Figs. 5(a) and (b). In Fig. 5(a), which shows the data for the \( ^{12}\text{C} \) t-2LG, the frequency hardening followed by a saturation at around \(-1 \) V for the LG and HG modes is evident, and means that the phonon self-energy renormalization is taking place and is a major effect between \(-1 \) V and 0 and from \(-1 \) V on, the doping-related changes in the C-C bonds, which decrease the phonon frequency, is a major effect. No band gap is introduced since the 2LG in question is turbostratic. Now, as shown in Fig. 5(b), the LG and HG frequencies decrease for the \( ^{12}\text{C} \) AB-2LG, which means that the changes in the C-C bonds are the major changes, as explained above. For negative electrochemical potentials, in which electrons are being injected to the system, \( E_{p} \) will be in the conduction band before the condition \( E_{\text{ph}} < E_{\text{gap}} \) occurs\(^{21} \). This means that the band gap will not play an important rule for negative potentials. For the range from 0 to \(+1 \) V, the frequency is roughly constant for the HG mode in Fig. 5(b) and slightly increases for the LG mode. This suggests that the band gap is likely affecting the LG mode which is halting the phonon renormalization, since when \( E_{p} \) decreases (meaning that the system is doped with holes) the electrons supposedly going from the \( \pi_{1} \) band to the \( \pi_{1}^{*} \) band will eventually fall into the band gap. During the time this happens, the C-C bond changes will be the major effect in the frequency changes (note that the frequency should increase according to Lazzeri et al.\(^{21} \)). Additionally, we believe that the inhomogeneous charging of the top and bottom layers in AB-2LG could explain why the band gap almost does not affect the HG mode\(^{21} \). Finally, at high positive potentials above \(1 \) V, the explanations given above are enough to explain the frequency changes since the gap will not affect the system anymore. Moreover, since the t-2LG system does not open a band gap, its frequency behavior (see Fig. 5(a)) with the electrochemical potential is totally explained within the phonon self-energy formalism and together with C-C bond changes.

In conclusion, we studied \( ^{12}\text{C} \) AB-2LG by Raman spectroscopy and in situ Raman spectroelectrochemistry. A mass-related symmetry breaking is observed where the \( ^{12}\text{C} \) AB-2LG exhibits two distinct G modes, one LG and another HG, which are related to a symmetric (LG) and anti-symmetric (HG) combination of \( E_{p} \) and \( E_{u} \) modes existing in the \( ^{12}\text{C} \) AB-2LG, where no mass-related symmetry breaking takes place. Indeed, this mode mixing happens due to a mass-related symmetry breaking of the inversion symmetry usually present in the unit cell of AB-2LGs. In the case of \( ^{12}\text{C} \) AB-2LG, this symmetry is naturally broken since the top atoms in the unit cell are \( ^{13}\text{C} \) atoms and the bottom atoms in the unit cell are \( ^{12}\text{C} \) atoms. This is different from \( ^{12}\text{C} \) t-2LG, where the two distinct LG and HG modes are related to the \( E_{p} \) modes from the \( ^{13}\text{C} \) and \( ^{12}\text{C} \) individual layers, respectively. In \( ^{12}\text{C} \) AB-2LG, the electrochemical charging reflects a smaller sensitivity of \( E_{p} \) to the electrode potential due to the effect of the modified electronic structure as compared to that for \( ^{12}\text{C} \) t-2LG. In addition, spectroelectrochemical experiments in AB-2LG indicated more charge on the top layer than on the bottom layer.

**Methods**

**Graphene flakes synthesis.** The AB stacked 2LG was prepared using a modified CVD growth method. A thick copper foil (127 mm thick, 99.9%, Alfa Aesar) forming an enclosure over the growth zone was used as a catalyst which was cleaned by dipping the copper into 

**Raman spectroscopy.** For the doping experiments, the graphene samples on a SiO\(_2\)/Si substrate served as working electrodes and the samples were contacted using Au evaporated on a part of the substrate. The cell was completed with a Pt-counter electrode and an Ag-wire pseudo-reference electrode. The electrolyte solution used was 0.1 M LiClO\(_4\) dissolved in dry propylene carbonate/PMMA (Aldrich). Electrochemical doping of the working graphene electrode was carried out by varying the applied potential between \(-1.5 \) and \(+1.5 \) V vs. an Ag pseudo-reference electrode (PAR potentiostat). We used a three electrode system and carried out measurements in the potentiostatic regime, so that no current was flowing through the reference electrode during the measurements. Care was also taken so that the current flow through the working electrode was minimal. Since the state (potential) of the pseudo-reference electrode is not changed during the measurement, the applied potential on the working electrode is well defined. The Raman spectra were excited by a 532 nm diode laser (Coherent). The spectrometer resolution was about 2.5 cm\(^{-1}\). The spectrometer was interfaced to a microscope (Carl-Zeiss, objective 100×). The size of the laser spot was about 1 μm.
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Acknowledgments
This work was supported by the Czech Ministry of Education, Youth and sports (LH-13022), and Czech Grant agency (P208-12-1062). The work done at MIT has been supported by NFS-DMR 10-04147. D.L.M. acknowledges the Brazilian agency CNPq.

Author contributions
M.K. performed measurements. P.T.A. and M.K. analyzed and explained the data. P.T.A. and M.K. wrote the manuscript. O.F., D.L.M., W.F., J.K. and M.S.D. discussed and reviewed the manuscript contents.

Additional information
Competing financial interests: The authors declare no competing financial interests.

How to cite this article: Araujo, P.T. et al. Mass-related inversion symmetry breaking and phonon self-energy renormalization in isotopically labeled AB-stacked bilayer graphene. Sci. Rep. 3, 2061; DOI:10.1038/srep02061 (2013).

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