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The existence and stability of two dimensional (2D) materials has been a long-debated subject. Graphene, a purely one atom thick 2D material formed by carbon atoms arranged in a honeycomb lattice, was presumed not to exist because strictly two dimensional materials are thermodynamically unstable [1–3]. The recent discovery of graphene [4, 5] has raised renewed interest regarding the stability of 2D materials. Here by comparing the properties of exfoliated and epitaxial graphene under soft X-ray radiation, we show that in single layer exfoliated graphene (a closer analogue to 2D material), the in-plane carbon-carbon bonds are unstable under X-Ray radiation. This is evidenced by the decrease in the absorption edge of the σ^* orbital and the strong enhancement of the Raman D peak, pointing to the formation of smaller in-plane crystallites. On the contrary, the effect of X-ray radiation on epitaxial graphene is negligible due to the stronger interaction with the substrate. Our results demonstrate the importance of the interaction along the third dimension in stabilizing the long range in-plane carbon-carbon bonding, and suggest the possibility of using X-ray to pattern graphene nanostructures in exfoliated graphene.

According to the Mermin-Wagner theorem [1], long-range magnetic order could not exist in one or two dimensions because the long-range order can be easily destroyed by long wavelength fluctuations. This was later extended to the crystalline order in purely flat 2D membranes [2]. However, by breaking the flatness of the membrane, e.g. through strong height fluctuations, the 2D membrane can still remain stable. A beautiful example of this has been recently found in graphene. It was reported that a free standing isolated graphene membrane does not remain flat but is intrinsically corrugated [6] and the degree of corrugation decreases as the number of graphene layers increases [7]. It has been proposed that this curvature is indeed crucial for the stability of 2D graphene [6, 8, 9] and is likely due to multiplicity of chemical bonding of carbon.

Here we present the first experimental evidence of the important role of the interaction along the third dimension in stabilizing the long range carbon-carbon (C-C) bonds in graphene. In particular we show that single layer exfoliated graphene is unstable under soft X-ray exposure, resulting in the local breaking of the sp^2 bonding and the formation of small crystallites within the sample. As the interaction along the third dimension increases, either by increasing the sample thickness or through stronger bonding with the substrate,

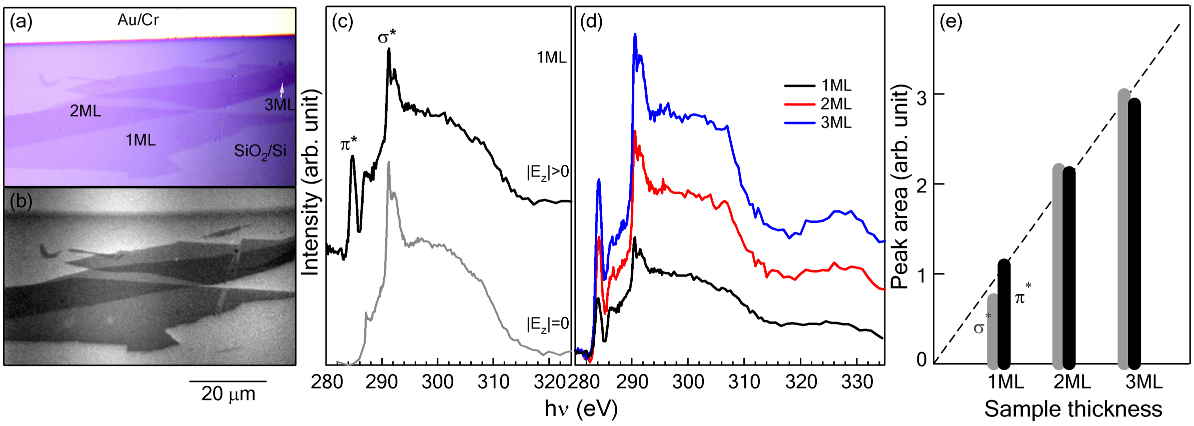

FIG. 1: **Optical and photoemission microscopy images for exfoliated graphene.** (a) Optical image of a representative exfoliated sample under study with different sample thickness. The electrical contact to the graphene samples is provided by a region of Au/Cr electrode (light yellow regions on the top of panel a) deposited on the SiO_2. (b) PEEM image of the same sample taken at photon energy of 279 eV, right before the C 1s absorption edge. Strong intensity contrast between regions of single layer, bilayer and trilayer graphene can be observed directly in both panels. The spectra are normalized by the spectrum from Au on the same wafer. (c) C 1s spectra taken on single layer exfoliated graphene with zero (gray curve) and non-zero (black curve) out-of-plane polarization components (E_z) respectively. (d) C 1s spectra taken from single layer, bilayer and trilayer graphene with non-zero out-of-plane polarization. (e) Area of the π^* and σ^* peaks as a function of the sample thickness extracted from data shown in panel d, after subtraction of a smooth background.

as in the case of epitaxial graphene, the sp^2 bonds become more stable. This study has been possible by combining the advantages of two spectroscopies: Raman, a convenient probe for determining the amount of disorder, edge states and the breaking of C-C bonds [10, 11] and X-ray absorption spectroscopy (XAS) at the C 1s edge, a direct way of detecting sp^2 bonding, as it directly involves the excitation of electrons from C 1s core level to partially filled and empty states [12].

Figure 1 (a) shows the optical image of a typical exfoliated sample. Clear optical constrast can be observed between regions of graphene with different sample thickness [5]. Figure 1(b) shows the photoemission electron microscopy (PEEM) image taken at 279 eV photon energy before the C 1s K edge on the same sample. The capability of spatial resolution in PEEM experiments, down to tens of nanometers, allows an easy detection of each graphene region with different sample thickness. Strong intensity contrasts between different pieces are observed. Similar to the optical image (panel a), it is clear that as we move from the Si/SiO$_2$ substrate to single layer and to thicker graphene samples, the X-ray absorption increases resulting in darker region. Figure 1(c) shows the C 1s XAS spectra taken on single layer exfoliated graphene with two different polarizations. The two main features at ≈ 285 eV, and at ≈ 292 eV, correspond respectively to the π^* orbitals at the K and M points of the Brillouin zone and to the σ^* orbitals at the Γ point [13]. Their in-plane and out-of-plane character is confirmed by the dependence from the polarization of the incident photons (panel c) [13]. More specifically, when the light polarization is in-plane, only the in-plane σ^* obital at 292 eV contributes to the C 1s edge, while when the out-of-plane polarization component increases, the intensity of the π^* feature at 285 eV strongly increases.

In Figure 1(d) we show the C 1s spectra of exfoliated graphene for different sample thickness. As in panel c, the π^* feature and the splitting of the σ^* orbitals are observed in all the spectra, independent of the sample thickness. The main difference is that as the thickness increases, the intensity of the σ^* and π^* features increases. This is due to the increase of available trasitions into other regions of the Brillouin zone between other σ^* or π^* states, similar to those observed in graphite [13]. The better energy resolution and likely sample quality of this experiment has allowed us to clearly resolve these two peaks, not observed in a previous study [14], and hence to quantify the thickness depedence of the absorption spectra and directly compare it to the optical reflectivity data. In panel e we show the absorption intensity, determined from the area underneath the π^* and σ^* orbitals near the C K edge. The data clearly show that the intensity of the π^* and the σ^* orbitals scales linearly with the sample thickness for up to three layers. Interestingly, this is in close analogy to the quantized steps observed in optical reflectivity and transmission for different graphene thickness [15, 16], which are defined only by the fine structure universal constant $\alpha = e^2/\hbar c$ [16]. This result suggests that, even at such high energies the universality still holds and the absorption spectra is still related to the universal constant α, the parameter that defines the optical transparency of graphene.

Figure 2 shows the time evolution of the absorption spectra for exfoliated (panels a-c) and epitaxial (panel d) graphene. The relative intensity ratio of the σ^* to the π^* orbital show

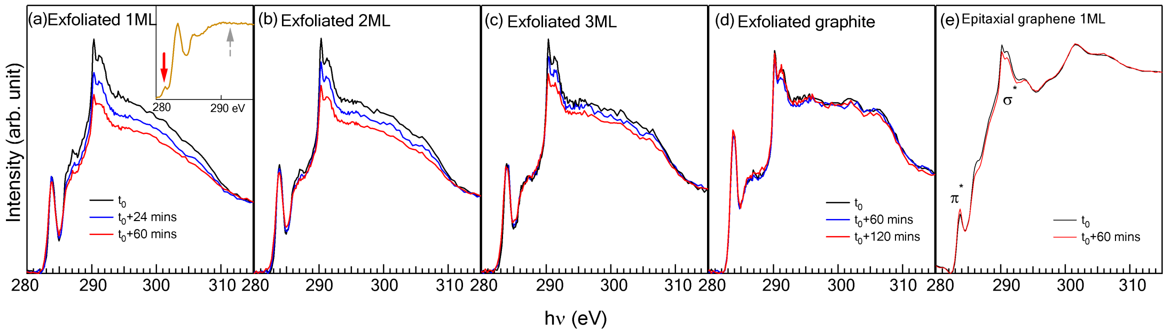

FIG. 2: **Effects of X-ray radiation on the absorption spectra of exfoliated and epitaxial graphene.** Time dependence of the C 1s XAS for (a) single layer (b) bilayer and (c) trilayer exfoliated graphene (d) exfoliated graphene and (e) epitaxial single layer graphene. The spectra are offset to have zero in the pre-edge and normalized to the same value at 315 eV for each sample. The inset in panel a shows an extreme sample which has negligible σ^* signal (pointed to by the gray arrow) after radiation and additional pre-edge peak (pointed to by the red arrow) which is likely asscoiated with edge states.

a clear time dependence from X-ray exposure. More specifically, the time evolution of the spectra is strongest for exfoliated single layer graphene (panel a), as measured from the 24% change in the intensity ratio of the σ^* orbital to the π^* orbital, and decreases significantly as the number of layer increases, from 20% in bilayer to 15% in trilayer graphene. These findings suggest a strong radiation-induced damage of the exfoliated graphene upon soft X-ray, a surprising result considering the inert character of carbon. This is reminiscent of the radiation induced damage observed in biological carbon reach samples [17]. We note that, although the results here presented are reproducible for all the samples studied (five in total), in some cases the absorption spectra of single layer graphene shows more dramatic changes. In an extreme case (inset in panel a), the signal of the σ^* orbital completely disappeared and an additional peak arised before the adsorption edge (pointed to by a red arrow) reminiscent of the edge states observed in nanographite sample [18].

The strong radiation-induced change of the single layer exfoliated graphene (panel a) is in contrast to the much weaker effect on the epitaxial single layer graphene (panel d). As for the exfoliated sample, the π^* and σ^* peaks can be still clearly resolved in the epitaxial sample and appear at similar energies (panel d), a further confirmation that the overall electronic structure of epitaxial and exfoliated graphene is similar in nature, although additional

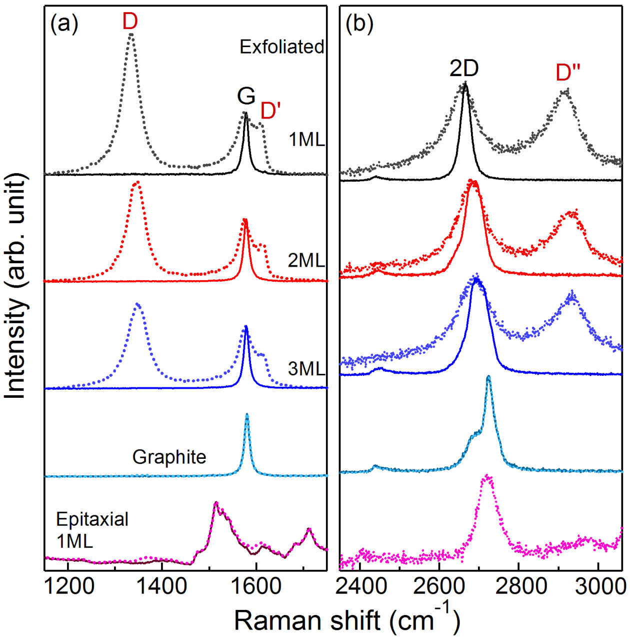

FIG. 3: **Effects of X-ray radiation on the Raman spectra of exfoliated and epitaxial graphene.** Raman spectra for epitaxial samples with different sample thickness (1ML, 2ML, 3ML and graphite) and single layer epitaxial graphene with laser excitation wavelength of 512 nm (Coglar, please correct it if this is wrong.). The solid and the dotted curves are taken before and after X-ray radiation. The spectra are normalized to have the same amplitude for the G peak and 2D peak.

peaks attributed to the SiC substrate appear in the C 1s absoprtion spectrum. However, in striking contrast to the single layer exfoliated sample (panel a) we find that in the epitaxial sample the absorption spectrum is very stable and no significant changes are observed within a much longer interval of time. The direct comparison excludes any type of artifacts of the experiments, as the two samples were measured in the same chamber under the same conditions. Instead it suggests that X-ray radiation induces different effects on the exfoliated and epitaxial graphene samples, which is most likely associated with their intrinsic properties, e.g. the different strength of interaction along the third dimension between these two types of samples.

To better understand the origin of this radiation-induced change, we performed Raman measurements on the same samples before and after exposure to soft X-ray. The comparison is shown in Figure 3. Before exposure, the exfoliated graphene sample shows a sharp G peak induced by the zone center E_{2g} phonon at ≈ 1570 cm^{-1}, and a strong 2D peak (overtone of the zone boundary A_{1g} phonon) at ≈ 2700 cm^{-1}. The 2D peak in single layer graphene shows a single component, while the 2D peak for bilayer, trilayer and infinite layers graphene is broader and contains multiple components, in agreement with previous studies [19, 20]. The sharpness of the G and 2D peaks, as well as the absence of the disorder-induced D peak at $\approx$ 1360 cm^{-1} [10, 11, 21], shows that the samples under study are of very high quality, and the amount of disorder is negligible. However, after X-ray exposure, the Raman spectra show significant changes in all the exfoliated samples, although the degree of change decreases from single layer to trilayer graphene and almost disappear for infinite layer graphite. More specifically, we observe the appearence of a huge D peak at 1360 cm^{-1}, as well as the appearance of the D$'$ peak at 1620 cm^{-1} and D$''$ peak at ≈ 2950 cm^{-1}, accompanied by the broadening of both the G (1570 cm^{-1}) and 2D (2700 cm^{-1}) peaks. The appearence of the D and D$'$ peaks in the Raman spectra in fact, is related to an increase of disorder and/or breaking of the carbon bonds [10, 11, 20–22]. In particular, a recent spatially resolved Raman study on exfoliated graphene has shown that the D peak is mostly visible at the boundaries of the sample while is barely resolved in the middle of the sample [20], suggesting that the D peak is dominated by edge states. Moreover, it has been shown that the D peak is a good indication of the crystallite size as its intensity increases in samples with smaller crystallites [10, 11]. In line with the absorption results (see Figure 2), the comparison between different thicknesses suggests that the biggest radiation-induced changes occur on the single layer exfoliated graphene sample. On the contrary, the Raman spectrum for the single layer epitaxial graphene shows negligible change, although it has been radiated for a much longer time ($\approx$ 10 hours), once again pointing to the different nature between exfoliated and epitaxial graphene and a better stability of the latter to X-ray radiation.

The results here presented point to a scenario where the X-rays locally break the sp^2 bonding (see schematic drawing in Figure 4), giving rise to small crystallites within the same graphene sheet. This is supported by the big changes observed in the Raman spectra after X-ray exposure (Figure 3), together with the decrease of the σ^*-orbital-related signal in the absorption spectra (Figure 2), and the appearence of a broad pre-edge feature (inset of figure 2a) similar to that observed in nanographite edges [18]. As shown above, such radiation-induced bond-breaking effect decreases when the interaction along the third dimension increases either by increasing the number of layers (also supported by the decreased

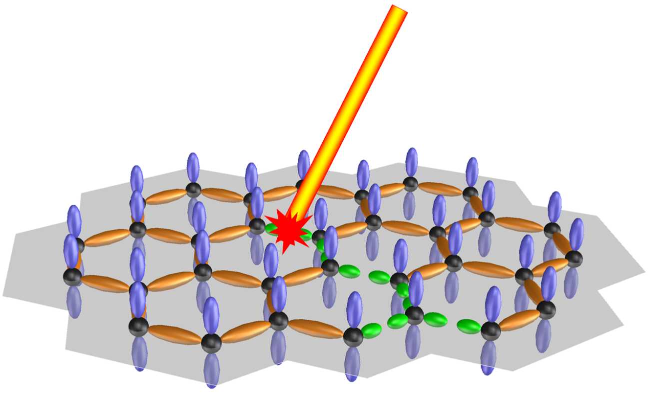

FIG. 4: **Scehmatic drawing to show the breaking of carbon-carbon bonds by X-ray radiation.**

intensity of the pre-edge feature [14]) or through a stronger interaction with the substrate, which helps to stabilize the long range order in the 2D graphene. The average crystallite size L can be estimated from the ratio between the G and D peaks in the Raman spectra, $L(nm) = 2.4 \times 10^{-10} \lambda_{laser}^4 \frac{I(G)}{I(D)}$ [11], where λ_{laser} is the laser excitation wavelength in unit of nm. In the case of single layer exfoliated graphene, I(D)/I(G)=2.3 with λ=512 nm, leading to an average crystallite size of 7 nm which increases increases, as the number of layer increases, from L=10 nm for bilayer graphene to L=12 nm for trilayer graphene.

In summary, we found that single layer exfoliated graphene is unstable to soft X-ray exposure, resulting in local breaking of the sp^2 bonding and the formation of small crystallites within the sample. As the interaction along the third dimension increases, either by increasing the sample thickness or through stronger bonding with the substrate, as in the case of epitaxial graphene, the graphene sample becomes more stable. These results point to the crucial role of the interaction along the third dimension in stabilizing quasi-two dimensional graphene. Finally, this ability to easily break the carbon-carbon bonds suggests the possiblity of using X-rays or even lasers [23] to "write" graphene nanostructures, an easier alternative to standard writing techniques.

Methods

The experiments have been carried out on two different types of samples: exfoliated graphene on Si/SiO$_2$ and epitaxial graphene on SiC. The thickness of exfoliated graphene samples is characterized by optical contrast [15, 16] and confirmed by Raman measurements [19, 20] prior to the XAS measurements. The thickness of epitaxial graphene is characterized by low energy electron microscope (LEEM) [24]. Although in both types of samples the overall electronic structure of graphene is preserved, they are characterized by different strength of interaction with the substrate and hence by different degrees of interaction along the third dimension. For exfoliated graphene [4, 5] the interaction occurs only through weak van der Waals force, while for epitaxial graphene, obtained by thermal decomposition of the SiC substrate [25], the interaction is much stronger. This is manifested by the formation of a first carbon rich layer strongly bounded with the SiC substrate, with the same crystallographic structure of graphene but only σ bands [26], and the opening of a gap in the π bands at the Dirac point for the first graphene layer (second carbon layer) [27–30], absent in the case of exfoliated graphene [31, 32].

X-ray absorption spectroscopy (XAS) spectra at the C 1s edge were taken with photoemission electron microscope (PEEM) at PEEM2 of the Advanced Light Source (ALS) in Berkeley. The microscope is operated in the total electron yield (TEY) mode by recording the intensity maps while sweeping the photon energy across the C K edge. The photon flux is cut down to only 1/3 of the regular value to decrease the X-ray radiation damage on the sample. The Raman spectra were taken with ...

Acknowledgments

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