Enhancing the adhesion of graphene to polymer substrates by controlled defect formation

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Abstract
The mechanical integrity of composite materials depends primarily on the interface strength and the defect density of the reinforcement which is the provider of enhanced strength and stiffness. In the case of graphene/polymer nanocomposites which are characterized by an extremely large interface region, any defects in the inclusion (such as folds, cracks, holes, etc) will have a detrimental effect to the internal strain distribution and the resulting mechanical performance. This conventional wisdom, however, can be challenged if the defect size is reduced beyond the critical size for crack formation to the level of atomic vacancies. In that case, there should be no practical effect on crack propagation and depending on the nature of the vacancies the interface strength may in fact increase. In this work we employed argon ion ($\text{Ar}^+$) bombardment and subsequent exposure to hydrogen ($\text{H}_2$) to induce (as revealed by x-ray and ultraviolet photoelectron spectroscopy and Raman spectroscopy) passivated atomic single vacancies to CVD graphene. The modified graphene was subsequently transferred to PMMA bars and the morphology, wettability and the interface adhesion of the CVD graphene/PMMA system were investigated with atomic force microscopy technique and Raman analysis. The results obtained showed clearly an overall improved mechanical behavior of graphene/polymer interface, since an increase as well as a more uniform shift distribution with strain is observed. This paves the way for interface engineering in graphene/polymer systems which, in pristine condition, suffer from premature graphene slippage and subsequent failure.

Supplementary material for this article is available online

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(Some figures may appear in colour only in the online journal)

1. Introduction

Graphene, an emerging nano-carbon material of atomic thickness \cite{1} shows considerable promise in structural composite applications thanks to its unique combination of high tensile strength, Young’s modulus \cite{2} and structural flexibility \cite{3,4}, which arise due to its structural (2D) perfection and its high strength and stiffness of the covalent C–C bonds \cite{5}. Furthermore, thin sheets of graphene are amenable to new textural modifications such as those inspired by Japanese Kirigami \cite{6}, which could be stretched up to 240% of their initial length and bent using the radiation pressure of a laser beam or twisted with a magnetic field without breaking.
The excellent mechanical [7, 8], electrical [9, 10], as well as, thermal [11] properties of graphene can be put to good use when graphene is combined with other materials such as engineering plastics. In most semi-industrial scale applications [12–14] graphene is incorporated in the form of exfoliated flakes of μm dimensions but the obtained results are often limited by the small lateral size and ineffective dispersion [15, 16]. One way to tackle these problems particularly in certain applications, is to employ CVD-grown graphene [17, 18] that could be produced in either large or even continuous (roll-to-roll) sheets [12, 14] that can be incorporated on the top of polymer substrates or even embedded into polymer matrices [19].

However, in this case the graphene sheets contain structural imperfections such as a network of wrinkles, cracks and folds [20–25], which can generally be defined as defects [26–30] and impair somewhat the properties of the finished products. According to Han et al [31], the onset of crack nucleation occurs near the presence of defects, determine graphene’s performance under tensile loading. Moreover, the low interfacial adhesion between graphene and polymer due to the weak van der Waals bonding is still a problem that can lead to premature failure of CVD graphene/polymer systems at small strains [32]. Nevertheless, deviations from the perfect atomic arrangements in graphene play an important role in affecting its performance [19, 33–35], as they make it possible to tailor its local properties in cases where it is applied as a multi-functional coating [3, 36] in polymer matrices [37–40] for various composite applications [12, 14, 41–44] and to achieve new functionalities [45, 46].

The most frequently employed polymer is the poly-(methyl methacrylate) (PMMA), which is used as a substrate for graphene transfer and as a matrix for device fabrication. Compared to other typical polar molecules, such as polycarbonate or, even water, PMMA is a long-chain molecule with strong dipole interaction with graphene (attractive inter-surface forces such as van der Waals forces). Density functional theory calculations have shown that PMMA radicals may form covalent bonds with a graphene defects, which usually appeared in grain boundaries. In particular, the local re-hybridization of carbons causes sp² to sp³ transitions; thus, modifying graphene’s band structure near the Fermi level [47].

Several strategies are proposed to modify the graphene surface in order to strengthen the interfacial adhesion [48–50]. Generally, irradiation by electron beam [51], or by ultraviolet (UV) radiation [52] or by ion radiation at room temperature gives rise to a continuous formation of defects and leading eventually to the development of holes and amorphization.

Among them, argon (Ar⁺) ion bombardment is the most studied method and the defects are quantified mainly with Raman spectroscopy [53–55]. It has been found that when a population of defects is generated in a graphene sheet by irradiation and then is exposed to hydrogen, dissociative adsorption of hydrogen molecules is possible to occur [56]; thus, a better interfacial adhesion [45, 46] can be attained. In this context, it has been suggested that this dissociative adsorption of hydrogen molecules occurs on a graphite surface at vacancies [57] and at the armchair edge of graphite [58].

Based on the above a method to improve the interfacial adhesion between CVD graphene/PMMA is proposed herein. The main idea is to create a uniform network of atomic vacancies beyond the critical size for any crack or dislocation propagation. These vacancies can be treated (passivated) by chemical means in such a way that can act as anchors between graphene and surrounding polymer and thus enhance the interfacial adhesion. As presented below, the defects are created in an ultra high vacuum chamber (UHV) by Ar⁺ bombardment on a CVD graphene grown on copper (Cu) substrate and the defected samples are exposed to H₂.

Such a procedure leads to a high density of defects on graphene surface [54] which can be identified by a variety of analytical techniques such as x-ray photoelectron spectroscopy (XPS). Furthermore, contact angle measurements showed that this procedure also leads to more hydrophobic surfaces, while Raman analysis along with atomic force microscopy (AFM) topography are employed for assessing the strain distribution in the graphene.

2. Experimental

2.1. Synthesis of CVD graphene grown on Cu

CVD synthesis of graphene was performed in an AIXTRON® (Black Magic) CVD chamber. Copper foils supplied from JX Nippon Mining & Metals® with a purity of 99.95% were used as the catalyst substrates. Before the introduction of the copper foil into the CVD chamber, the foil was cut into 7 × 7 cm² and cleaned by isopropanol to remove any organic contamination. After the closure of the chamber, the foil was heated in 1000 °C in argon/hydrogen atmosphere and was kept there for 5 min for annealing. Then, the hydrogen flow was terminated, temperature was decreased until 925 °C and at the same time methane was introduced into chamber, as carbon feedstock to initiate the graphene growth on copper foil surface. After 5 min at 925 °C, the chamber was cooled down to 650 °C, where the methane flow was terminated. Finally, the chamber was cooled gradually to room temperature.

2.2. Ar⁺ ion bombardment

The CVD graphene/Cu samples were introduced in UHV chamber and subjected to Ar⁺ bombardment without previous treatment in order to avoid changing its pristine properties. The only parameter which was varied was the ion energy, from 35 up to 200 eV, while the Ar⁺ pressure, the irradiation time and the spot were constant. The Ar⁺ pressure was 3 × 10⁻⁶ mbar, the duration 12 s, the distance between the sputtering gun and the sample was 6 cm while the spot size was a circle with 7 mm diameter. Subsequently after irradiation, the samples were exposed to hydrogen atmosphere (1 bar) for 10 min in the high pressure chamber.
2.3. Samples’ preparation and transfer to polymer substrates

The modified graphene surfaces were transferred on a PMMA substrate. Both pristine and treated CVD graphene/Cu samples were transferred from the copper foil to a PMMA substrate, by implementing a ‘dry transfer’ method. The steps of the method are shown schematically in figure S2, which is available online at stacks.iop.org/NANO/30/015704/mmedia. With this method, graphene was actually transferred to the desired position, on the PMMA substrate, just before the removal of copper. Initially, a thin layer of PMMA ∼200 nm (495k, 3% in anisole) was spin-coated on graphene and copper. After that, the graphene sample with the PMMA coated film and the PMMA substrate, were pressed for a couple of hours. Then, the uncoated graphene (back side of the copper foil) was removed by using O2 plasma and the copper foil was etched by 0.15 M ammonium persulfate (APS) solution. Finally, the sample was replenish with de-ionized water and dried under N2 flow.

2.4. Characterization by implementing XPS/UPS

The surface analysis studies were performed in a UHV chamber (P < 10−9 mbar), which consists of a three chambers: (a) a high pressure chamber, where exposures of samples for gas pressure up to several atmospheres takes place, (b) a preparation chamber, where the ion gun for Ar sputtering is placed and (c) an analysis chamber. The analysis chamber is equipped with a SPECS LHS-10 hemispherical electron analyzer, a dual-anode x-ray source for XPS and a UV source (model UVS 10/35) for UPS measurements.

The XPS measurements were carried out at room temperature using monochromatized AlKα radiation under conditions optimized for maximum signal (constant ΔE mode with pass energy of 36 eV giving a full width at half maximum (FWHM) of 0.9 eV for the Au 4f7/2 peak). The analyzed area was an ellipse with dimensions 2.5 × 4.5 mm². The XPS core level spectra were analyzed using a fitting routine, which can decompose each spectrum into individual mixed Gaussian–Lorentzian peaks after a Shirley background subtraction. The UPS spectra were obtained using HeI irradiation with hν = 21.23 eV produced by a UV source (model UVS 10/35). During UPS measurements the analyser was working at the constant retarding ratio (CRR) mode, with CRR = 10. The work function (WF) was determined from the UPS spectra by subtracting their width (i.e. the energy difference between the analyzer Fermi level and the high binding energy cutoff), from the HeI excitation energy. For these measurements a bias of −12.30 V was applied to the sample in order to avoid interference of the spectrometer threshold in the UPS spectra.

2.5. Raman measurements

In order to check the influence of the morphology of the substrate on graphene properties, Raman mapping took place. Spectra were taken with 514 nm (2.41 eV) laser using a MicroRaman (InVia Reflex, Renshaw, UK) set-up. The laser power was kept below 1.5 mW on the sample to avoid laser-induced local heating, while an Olympus MPLN100x objective (NA = 0.90) was used to focus the beam on the samples. The obtained spectra of the pristine and treated CVD/PMMA system are presented in figure S5.

2.6. Contact angle measurements

The contact angle of water drops on the surface of graphene/Cu samples were measured as follows: a droplet of the liquid was deposited by a syringe which was positioned above the sample surface and the image captured by a high resolution stereomicroscope (Nikon SMZ1000) was analyzed to determine the contact angles.

2.7. Mechanical tensile tests

2.7.1. Quasi-static deformation. The top surface of the monolayer CVD graphene/PMMA system was subjected to tension using a four-point bending apparatus. A more detailed description of the mechanical testing applied is presented elsewhere [59]. In order to conduct Raman mapping during loading, the four-point bending apparatus was placed on a three-axis piezoelectric translation stage that was operated on three orthogonal axes by a ThorlabsInc. piezoelectric controller. The NanoMax three-axis flexure stage can provide nano-metric positioning on the three orthogonal axes. At each strain level, the stage was translated with a step of 5 μm with the simultaneous collection of Raman spectra within an area of 15 × 15 μm² (16 total points) for both examined systems.

2.8. AFM measurements

AFM images were collected by a contact mode (Bruker, Dimension-Icon). Images were obtained using ScanAsyst-Air probes (silicon tips on silicon nitride cantilever, Bruker) with 0.4 N m⁻¹ nominal spring constant of the cantilever.

3. Results and discussion

3.1. Modification of the CVD graphene sheets

Since the monolayer graphene is only 0.3 nm thick [60, 61], surface sensitive methods, such as XPS, provide valuable information about the changes on graphene before and after irradiation. The defects on a CVD mono-layer graphene on Cu are implemented by Ar⁺ ions irradiation in an UHV chamber. In order to avoid possible contamination of the defect sites of the irradiated surfaces during air exposure, the irradiated samples were subsequently exposed to H2 atmosphere.

It has been shown that hot hydrogen atoms (H) (i.e. with a few tens of eV) can be adsorbed on the basal plane of surface-clean graphene, while adsorption is barrier-less on free edges or vacancies (dangling bonds) [62]. In the present study, the effect of H2 exposure on the Ar⁺ irradiated CVD graphene/Cu is investigated and it was found that H adsorbed on the defect sites created by Ar⁺ irradiation, prevented
Table 1. Ar⁺ ion energy irradiation, number of impacts per cm², sp³/sp² ratio, work function (WF) and I(D)/I(G) ratio of the corresponding graphene’s Raman peaks for the pristine and treated CVD graphene/Cu surfaces.

| Ar⁺ energy (eV) | Number of Ar⁺ impacts/cm² | sp³/sp² | WF ± 0.05 (eV) | I(D)/I(G) |
|-----------------|---------------------------|---------|----------------|-----------|
| Pristine (0)    | —                         | 0.10    | 4.40           | 0.13 ± 0.03 |
| 35              | ~10¹³                     | 0.11    | 4.40           | 0.15 ± 0.05 |
| 65              | ~6 × 10¹³                  | 0.13    | 4.35           | 0.21 ± 0.09 |
| 100             | ~1 × 10¹⁴                  | 0.15    | 4.30           | 1.00 ± 0.32 |
| 120             | 1.5 × 10¹⁴                 | 0.17    | 4.30           | 3.36 ± 0.45 |
| 130             | 2 × 10¹⁴                   | 0.20    | 4.25           | 2.18 ± 0.54 |
| 200             | 6 × 10¹⁴                   | 0.23    | 4.20           | 0.96 ± 0.06 |

...continued...

Figure 2 shows the HeI UPS valence band spectra and the high binding energy cutoff, from the pristine and the treated CVD graphene/Cu surfaces, respectively. In figure 2(I), the region 0–12 eV consists mainly of three peaks: (i) at ~3 eV (labeled as A) attributed to π electrons (sp³ hybridization), (ii) at ~6 eV (labeled as B) assigned to 2π(π+ + σ) and (iii) at ~10 eV (labeled as C) assigned to 2π–2π hybridization [67]. No great differences seems to be present in the spectra for Ar⁺ energies of range 35–130 eV, whereas at 200 eV the peak at ~6 eV is decreased in comparison to the peak at ~10 eV, while a reduction of the density of 2π(π+ + σ) states (~3 eV) near the Fermi level is observed. These changes in the valence band are expected since the sp³ C–H defects in graphene depresses the delocalized π-electrons significantly.

oxygen contamination from air [63]. The details are presented in the supporting information.

Subsequently, a method to induce defects with a controlled density is developed, by adjusting the energy of the Ar⁺ that interact with the surface. The ion energy was changed by regulating the voltage of the anode in the ion gun, while the irradiation time remained constant (12s). The number of defects per cm² of the graphene area was calculated by measuring the surface current during Ar⁺ irradiation and assuming that each Ar⁺ ion interacts with one carbon atom. The corresponding results for each ion energy are shown in table 1 [64].

After each Ar⁺ energy irradiation and H₂ exposure in situ XPS-UPS and ex situ Raman measurements recorded. Figure 1 shows the deconvoluted C1s XP spectra for pristine (figure 1(a)), Ar⁺ irradiated and H₂-exposed CVD graphene/Cu samples for different Ar⁺ energies. In order to remove the background noise caused by inelastic electron scattering, a simple Shirley-type correction was introduced.

The C1s peaks are analyzed into four components at binding energies 284.70 ± 0.05 eV assigned to C=C sp³ bonds, at 285.60 ± 0.05 eV attributed to carbon atoms with sp³ hybridization and two components and at 286.70 ± 0.1 eV and 288.5 ± 0.1 eV assigned to C—OH and C—O=C—O bonds, respectively [65]. The Ar⁺ impact per cm² area has been directly correlated to the sp³/sp² ratio and the results are shown in table 1. The sp³/sp² intensity components ratio for the pristine sample is 0.10 corresponding to ~9% sp³, which comes into agreement with the results obtained by Luo et al [66].

Figure 2 shows the HeI UPS valence band spectra and the high binding energy cutoff, from the pristine and the treated CVD graphene/Cu surfaces, respectively. In figure 2(I), the region 0–12 eV consists mainly of three peaks: (i) at ~3 eV (labeled as A) attributed to π electrons (sp³ hybridization), (ii) at ~6 eV (labeled as B) assigned to 2π(π+ + σ) and (iii) at ~10 eV (labeled as C) assigned to 2π–2π hybridization [67]. No great differences seems to be present in the spectra for Ar⁺ energies of range 35–130 eV, whereas at 200 eV the peak at ~6 eV is decreased in comparison to the peak at ~10 eV, while a reduction of the density of 2π(π+ + σ) states (~3 eV) near the Fermi level is observed. These changes in the valence band are expected since the sp³ C–H defects in graphene depresses the delocalized π-electrons significantly.

Figure 1. Deconvoluted C1s peak of CVD graphene/Cu samples for (a) pristine sample and after irradiation and exposed to H₂ for Ar⁺ energies of (b) 35, (c) 65, (d) 100, (e) 130 and (f) 200 eV.

Figure 2 shows the cut-off of the high binding energy region, where the WF of graphene can be estimated by subtracting the width of the photoelectron spectrum from the photon energy. The WF of the pristine surface is 4.40 ± 0.05 eV in agreement with literature values for a pristine graphene [67]. For the irradiated surfaces, the WF is gradually decreased starting from 65 eV Ar⁺ energy irradiation and reaching the value of 4.20 ± 0.05 eV for 200 eV Ar⁺ energy (ΔWF = 0.2 eV).

It is known that the sp³ bonding of carbon surface terminated in hydrogen leads to a small decrease of the WF which arises from the formation of a C–H⁺ surface dipole layer and its magnitude is proportional to the surface coverage and the number of defects per cm² of the graphene area was calculated.
of hydrogen [68]. Thus, the slight decrease of the WF of the treated surfaces is an indication of low coverage by H of the defected sites.

The Raman spectra of the pristine graphene/Cu and the treated surfaces are showed in figure S2 in the supplementary. The Raman spectrum of graphene has the typical peaks of all carbon allotropes [69]. Briefly, the G and D peaks, around 1580 and 1360 cm\(^{-1}\) are due to the sp\(^2\) bonded carbons. The G peak corresponds to the \(E_{2g}\) phonon at the Brillouin zone (BZ) center (\(\Gamma\) point). The D peak is due to the breathing modes of six-atom rings and requires a defect for its activation. It comes from TO phonons around the BZ K point, and it is activated by an intra valley scattering process. The 2D peak is the second order of the D peak. The defect-activated D' peak comes from the LO branch of the phonon dispersion and is seen around 1620 cm\(^{-1}\).

The evolution of Raman spectrum follows the trend firstly reported by Cançado et al [54]; thus, the increase of bombardment dose is followed by the appearance and enhancement of the D peak (35–65 eV) and the subsequent increase of the ratio \(I(D)/I(G)\). As the applied ion-dose further increases, the D' peak rises and all Raman peaks broaden (∼120 eV). Due to broadening, the G and D' peaks tend to overlap and form a single wider and blue shifted peak, while a sharp decrease of the ratio \(I(D)/I(G)\) is observed (130–200 eV). Therefore, the decrease of the ratio \(I(D)/I(G)\) indicates here enhancement of disorder since the G peak incorporates in essence the disordered-induces D' peak. The cut-off dose for defect creation is ∼35 eV, whereas above ∼200 eV graphene is severely damaged.

Based on the obtained Raman spectra (figure S2(a), (b)) and the dependence of the ratio \(I(D)/I(G)\) versus the bombardment dose applied (figure S2(c)), the energy of 120 eV is selected (optimum energy applied), as a trade-off between the number of defected areas and their size [54], in order to further investigate the stress-transfer efficiency of defected graphene/PMMA system.

### 3.2. Evaluating the morphology and the interface integrity of the CVD graphene coating/PMMA system before and after the insertion of defects

The morphology and the interface integrity of the pristine and the treated CVD graphene/PMMA system was evaluated for several samples. Initially, AFM was employed for both systems, to assess the structure of the as supported CVD graphene at the nanoscale. As can be seen from AFM high resolution images (figure 3), two different morphologies appeared depending on whether or not they had been treated by Ar\(^+\) irradiation. The first region (figures 3(a), (c)) is relatively ‘flat’ while the second that has a ‘ragged’ appearance corresponds to the presence of folds without a preferred orientation (figures 3(b), (d)).

These areas seem to be created on Cu foil, at the cooling step of CVD process [70, 71] and then are transferred directly on PMMA bar during the transfer process (figure S3) (see also experimental section). The creation of folds presented in
Figure 3. Atomic force microscopy (AFM) images prior loading of (a) ‘flat’ region of pristine surface, (b) ‘rugged’ region of pristine surface, (c) ‘flat’ region of treated surface and (d) ‘rugged’ region of treated surface. At every image, (i) represents the characteristic topography for each region while (iv) denotes the magnified region within the black solid square in (i). Also, (iii) is the corresponding 3D AFM image of (iv) and (ii) is the adhesion force histogram. All the samples examined were irradiated with Ar\(^+\) ion energy of 120 eV, which corresponds to Ar\(^+\) impacts per cm\(^2\) of $1.5 \times 10^{14}$ Ar\(^+\)/cm\(^2\).
Figure 3. (Continued.)
figures 3(b) and (d) are very similar to the folds appeared on graphene oxide films due to applied biaxial compression [72]. The latter seems to be confirmed also for the samples examined by Raman measurements (table S1), as it will be discussed further in the text. Similar images obtained from other specimens are also presented in figure S5.

In addition to the topographical study, adhesion force measurements were also recorded. The obtained statistical analysis (histograms) of the adhesion forces show an unsymmetrical Gaussian distribution for the pristine (both for the ‘flat’ and ‘rugged’ areas) and more symmetrical for the treated graphene, respectively (figures 3(a)(ii) and (c)(ii)). Similarly, the maximum value of the Gaussian distributions is shifted from 3.22 nN at the pristine state to higher force values of 5.18 nN for the treated surface, respectively. Analogous behavior was observed for the ‘rugged’ regions (figures 3(b)(ii) and (d)(ii)), where the mean value of the adhesion force is increased from 2.85 nN for the pristine to 5.84 nN for the treated specimens, respectively.

Based on the analysis made by Jiang et al [73] (see also the supporting information), the adhesion energy between graphene and PMMA substrate can be measured by force spectroscopy mode of AFM, using the Maugis-Dugdale model [74]. As depicted in table 2, there is a great increase of the surface energy, reaching up to 115% and 66% for the ‘rugged’ and ‘flat’ regions, respectively. As it is stated Jiang et al [73], the surface roughness significantly affects the measured adhesion force (table 2). By introducing a controllable amount of defects, the graphene’s roughness; thus, affecting further its interaction with the PMMA substrate.

Such an increase of the adhesion force can only be attributed to the modification of the graphene surface by the insertion of defects followed by the H₂ exposure. It seems that such a functionalization improves the bonding between graphene and hydrophilic PMMA transfer film (see also Experimental and figure S3), as it is also confirmed by the macroscopic results obtained from the contact angle measurements (figure S4), where an increase of 10% is recorded (table 3).

The effect of the presence of defects in the wettability of graphene has been studied for oxygen plasma treated graphene on SiC [75]. As the density of defects induced by plasma treatment increases, the surface energy also increases due to the fact that the graphene become polar after creating polar O–H bonds leading to a hydrophilic nature. In our case, the passivation of treated graphene with hydrogen atoms results just the opposite. As it is stated by Wu et al [63], during the preparation of graphene sheets by thermal exfoliation of graphene oxide (GO), the presence of hydrogen is essential for de-oxygenation of GO as well for structural defects removal; thus, oxygen-containing groups, i.e. hydrophilic surface functionalities, lead to a formed graphene with superior properties.

By following Neumann’s model [76] (see also the supporting information) and by applying a water droplet (polar solvent) before and after the treatment, the obtained surface energy of graphene on Cu is reduced by 5.9% (table 3); thus, becoming less hydrophilic. Therefore, the changes observed on the wetting behavior of graphene seem to affect positively its interaction with the non-polar PMMA film during the transferring process; thus, better interactions with the PMMA substrate (bar), leading to different mechanical response to the external applied load, as it will be further discussed below.

Additionally, by analyzing the profiles of the most representative Raman peaks of graphene (2D, G and D) [77–79] for both graphene systems, it seems to lead to the same result. By carefully selecting the same sampling areas of 20 × 20 μm² presented in figure 4, a full Raman investigation (121 data points) from both systems are obtained (figures S6(a) and (b)). The statistical analysis of the above is presented in figure S7.

For both systems, Pos(2D) has a mean value of the order of ~2690 cm⁻¹, indicating the presence of compression and/or doping [59] (figures S7(a), (b)). If we reasonably consider that the Pos(2D) shift is due to the imposition of biaxial strain during the production process [80], the corresponding compressive biaxial strain calculated, using the sensitivity value +148 cm⁻¹% [80], varies between −0.07% and −0.06% for the pristine and treated system, respectively (table S3).

By correlating Pos(2D) versus Pos(G) as shown in figure S8, it can be argued that for the collected data points the mechanical loading dominates upon doping [77], since the majority of the points follow a linear relationship. Especially, for the case of the treated CVD graphene the least-squares fitted slope (~1.7) is greater than the corresponding for the pristine system (~1.4), implying a greater mechanical adhesion [59, 80].

As for the Raman linewidths, useful interpretations can be extracted regarding doping, strain, disorder and number of layers in graphene [82, 83]. For the pristine CVD synthesized graphene film, the corresponding value of FWHM(2D) (33.3 ± 4.2 cm⁻¹) (figure S7(b)) at rest is larger compared to exfoliated flakes (~24 cm⁻¹) [84] and the reasons for that are given elsewhere [84, 85]. However, there is a set of data points exhibiting values of FWHM(2D) greater than 33 cm⁻¹, corresponding to ~20% of the examined data points (figure S7(b)), which is attributed to bi-layer or even multi-layer islands (three layers or more) [86, 87], as it has been explained elsewhere [77, 86–90]. For the treated CVD synthesized graphene sheet, the increased value of FWHM(2D)
(figure S7(d)) occurs as a result of the defect insertion, as it is also confirmed in figure S2(a). Similar results are observed for the FWHM of the G peak (figures S7(g) and (h)).

In addition, the presence of defect-activated D band [54, 91] is relatively lower for the pristine case, as it is confirmed by the value of $\sim 0.50$ for the $I(D)/I(G)$ ratio (figure S7(i)). The latter indicates that the pristine examined system has indeed a small amount of disorder or defects [92, 93]. According to Cançado et al [54, 94], by the insertion of defects, (figures S2 and S6(b)) the intensity ratio of the D and G Raman peaks ($I(D)/I(G)$) increases (figures S7(i) and (j)), the $D'$ peak appears (figure S6(b)), and a broadening of all peaks is also observed (figures S2 and S6(b))[91]. By implementing a controllable defect insertion, the obtained corresponding value is of the order of $\sim 3$ (figure S7(j)).

Following the analysis of Eckmann et al [55], for the relative intensity of the D and $D'$ peaks (figure S9), it is suggested that the inserted defects, for the optimum energy $120 \text{ eV}$ (figure S2(c)), are actually single-vacancy defects, since the value of $I(D)/I(D')$ is of the order of $\sim 8.5$. Similar results were also obtained by Polin et al [95], who argued that graphene becomes stiffer by controlled defect creation. As it will be shown below, it seems that those vacancies are actually assisting graphene to interact better with the polymer substrate (PMMA bar), as it is proved by the increase of the adhesion force (figure 3).

### 3.3. Implementation of mechanical loading

The mechanical response for both pristine and treated CVD graphene/PMMA systems upon external deformation (up to 1.0%) for an area in the specimens of $15 \times 15 \mu m^2$ was investigated. Prior to loading the strain state of the examined specimens was identified within the allocated sampling areas and the residual compressive strain is presented in table S3.

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**Figure 4.** Strain rate maps for Pos(2D) of a $15 \times 15 \mu m^2$ sub-area during (a) loading and (b) unloading for the pristine CVD graphene/PMMA system. Due to the apparent diversity of strain rate values of Pos(2D), two group of points with low (Group A) and high (Group B) strain rates are depicted.

**Figure 5.** Strain rate maps for Pos(2D) of $15 \times 15 \mu m^2$ area during (a) loading and (b) unloading for the treated CVD graphene/PMMA system, where an averaged increase of the shift over strain is observed in comparison to the pristine case. At the same time a very small diversity of strain rate values of Pos(2D) is also clearly depicted. The Ar$^+$ ion energy irradiation took place at 120 eV, which corresponds to Ar$^+$ impacts per cm$^2$ of $1.5 \times 10^{14}$ Ar$^+/cm^2$. 

120 eV (figure S2(c)), are actually single-vacancy defects, since the value of $I(D)/I(D')$ is of the order of $\sim 8.5$. Similar results were also obtained by Polin et al [95], who argued that graphene becomes stiffer by controlled defect creation. As it will be shown below, it seems that those vacancies are actually assisting graphene to interact better with the polymer substrate (PMMA bar), as it is proved by the increase of the adhesion force (figure 3).
An important parameter that has been identified by us and others previously [37, 96–98] as an index of stress-transfer efficiency, is the Raman shift rate per strain for the two most common mentioned vibrational modes (2D and G). For exfoliated graphene/PMMA systems the maximum values recorded are in the range of 55–60 cm$^{-1}$/% for the 2D peak and ∼25 cm$^{-1}$/% for the mean value of the G peak [99]. For corresponding CVD graphene/PMMA systems the above values represent upper limits often difficult to attain due to the inherent morphological defects of the CVD-grown graphene [19, 34, 100]. In this context, strain rate maps extracted for both loading and unloading cycles can actually be considered as an indirect adhesion indicators, since the measured Raman variations shifts of Pos(2D) and Pos(G) are related with the ‘true’ strain transferred from the matrix to the inclusion.

During loading, a broad value range for the strain rate of Pos(2D) is observed for the pristine CVD graphene/PMMA system (figure 4(a)). Particularly, there is a group of points (Group A, figure 5(a)), for which the Pos(2D) is shifted to lower values at very low rates (from −5 to −15 cm$^{-1}$/%). However, there are other points (Group B), for which the strain rates reach −55 cm$^{-1}$/% [101], which is the upper limit as mentioned above and also confirmed by others [37, 97–99].

Similarly, the Pos(G) red-shifts at a rate of −6 to −3 cm$^{-1}$/% for Group A, while the points of Group B exhibit shifts of up to −17 cm$^{-1}$/% (figure S10(a)). Moreover, for Group B, splitting of both the G and 2D peaks are observed which are indicative of efficient loading of the inclusion [102, 103]. The latter is depicted in figure S11, where typical spectra from both point groups are presented for applied strain...
of 0.80%. During unloading, both groups of points are shifting back at similar shift rates as the loading curves indicating elastic behavior (figure 4(b), figure S10(b)).

On the contrary the treated CVD graphene/PMMA system exhibits on average a much higher and narrower distribution of Pos(2D) shift rates during loading (figure 6(a)), of $\sim 30 \text{ cm}^{-1}/\%$. Therefore, it can be stated that the overall interaction with the substrate is higher than to the cases prior to treatment and therefore the stress-transfer efficiency has been greatly improved. Similar results are obtained for the Pos(G) which shifts approximately by $\sim 10 \text{ cm}^{-1}/\%$ on average (figure S12(a)), very close to the value of $-14.7 \text{ cm}^{-1}/\%$ obtained elsewhere [37] for CVD graphene. During unloading (figures 5(b), S12(b)), all the points of the examined area are blue-shifting with almost the same strain rate for both bands.

Figure 6 shows the section analysis of AFM images prior and after loading for the pristine and treated CVD graphene, respectively. After loading, it seems that the treated graphene has returned to a great extent to its initial loading position, compared to the pristine specimen (figure S13). Furthermore, the statistical analysis of the relative change of surface’s height ($\Delta H/H_o$) prior and after loading, shows an asymmetrical Gaussian distribution for the pristine and more symmetrical for the treated graphene, respectively (figures 6(a)(iii) and (b)(iii)).

For the former, recent works suggests that the repetitive reforming and breaking of interaction at interface region would occur during sliding process for both van der Waals and H-bond interactions [104, 105]. In case of the treated system, the insertion of specific population of defects on the CVD graphene along with their covering by H atoms, affects its interaction with the PMMA surface to a greater and more homogeneous extent; thus, graphene interacts better with the polymer substrate caused by a strong interaction of the defects with the PMMA.

4. Conclusions

In this work, CVD graphene on Cu substrate is treated by inserting defects with a well-controlled population by Ar$^+$ bombardment in a UHV chamber, followed by subsequent exposure to hydrogen atmosphere. The treated surfaces were characterized by several techniques which revealed that hydrogen reacts with carbon at the defect sites and passivated the carbon atoms.

We have shown that a controlled generation of atomic defects to CVD graphene results in the moderate increase of the adhesion between graphene and a polymer substrate and leads to a more uniform strain uptake in reinforcing inclusion. Since graphene adheres to polymer substrates through weak van der Waals bonding, this approach paves the way for improving the mechanical behavior of the graphene/polymer interface and for eventually tailoring the mechanical properties of graphene. While the proposed method presented herein represents the interface of CVD graphene/PMMA, it can be applied to other 2D materials improving the interfacial mechanics of composite materials.

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References

[1] Novoselov K S, Geim A K, Morozov S V, Jiang D, Zhang Y, Dubonos S V, Grigorieva I V and Firsov A A 2004 Electric field effect in atomically thin carbon films Science 306 666–9

[2] Lee C, Wei X, Kysar J W and Hone J 2008 Measurement of the elastic properties and intrinsic strength of monolayer graphene Science 321 385–8

[3] Jang H, Park Y J, Chen X, Das T, Kim M-S and Ahn J-H 2016 Graphene-based flexible and stretchable electronics Adv. Mater. 28 4184–202

[4] Kim S J, Bora Lee K C, Kim Y and Hae Hong B 2015 Materials for flexible, stretchable electronics: graphene and 2D materials Mater. Res. 45 63–84

[5] Fasolino A, Los J H and Katsnelson M I 2007 Intrinsic ripples in graphene Nat. Mater. 6 858–61

[6] Blees M K et al 2015 Graphene kirigami Nature 524 204–7

[7] Young R J, Kinloch I A, Gong L and Novoselov K S 2012 The mechanics of graphene nanocomposites: a review Compos. Sci. Technol., 72 1459–76

[8] Vadukumpully S, Paul J, Mahanta N and Valiyaveetil S 2011 Flexible conductive graphene/poly(vinyl chloride) composite thin films with high mechanical strength and thermal stability Carbon 49 198–205
[9] Fiori G, Bonacorso F, Iannaccone G, Palacios T, Neumair D, Seabaugh A, Banerjee S K and Colombo L 2014 Electronics based on two-dimensional materials Nat. Nanotechnol. 9 768–79

[10] He F, Lau S, Chan H L and Fan J 2009 High dielectric permittivity and low percolation threshold in nanocomposites based on poly(vinylidene fluoride) and exfoliated graphite nanoplates Adv. Mater. 21 710–5

[11] Teng C-C, Ma C-C-M, Lu C-H, Yang S-Y, Lee S-H, Hsiao M-C, Yen M-Y, Chioo K-C and Lee T-M 2011 Thermal conductivity and structure of non-covalent functionalized graphene/epoxy composites Carbon 49 5107–16

[12] Bae S et al 2010 Roll-to-roll production of 30-inch graphene films for transparent electrodes Nat. Nanotechnol. 5 574–8

[13] Yamada T, Ishihara M and Hasegawa M 2013 Large area coating of graphene at low temperature using a roll-to-roll microwave plasma chemical vapor deposition Thin Solid Films 532 89–95

[14] Kobayashi T et al 2013 Production of a 100-m-long high-quality graphene transparent conductive film by roll-to-roll high-quality chemical vapor deposition and transfer process Appl. Phys. Lett. 102 1–4

[15] Andrea L, Konstantinos K-A, Xavier Diez B, Alessandro K, Emanuele T, Nicola Maria P, Giovanna De L, Loris G and Vincenzo P 2017 Evolution of the size and shape of 2D nanosheets during ultrasonication fragment 2D Mater. 4 025017

[16] Palermo V, Kinloch I A, Ligi S and Pugno N M 2016 Nanoscale mechanics of graphene and graphene oxide in composites: a scientific and technological perspective Adv. Mater. 28 6232–8

[17] Ago H 2015 CVD growth of high-quality single-layer graphene Frontiers of Graphene and Carbon Nanotubes ed K Matsumoto (Tokyo: Springer) pp 3–20

[18] Novoselov K S, Falco V I, Colombo L, Gellert P R, Schwab M G and Kim K 2012 A roadmap for graphene Nanoscale 4 25017

[19] Anagnostopoulos G et al 2016 Mechanical stability of flexible graphene-based displays ACS Appl. Mater. Interfaces 8 22605–14

[20] Zhu W, Low T, Perebeinos V, Bol A A, Zhu Y, Yan H, Tersoff J and Avouris P 2012 Structure and electronic transport in graphene wrinkles Nano Lett. 12 3431–6

[21] Kim K, Lee Z, Malone B D, Chan K T, Alemán B, Regan W, Gannett W, Crommie M F, Cohen M L and Zettl A 2011 Multiplex folded graphene Phys. Rev. B 83 245433

[22] Kim K, Artyukhov V I, Regan W, Liu Y, Crommie M F, Yakobson B I and Zettl A 2011 Ripping graphene: preferred directions Nano Lett. 12 293–7

[23] Wang Y, Yang R, Shi Z, Zhang L, Shi D, Wang E and Zhang G 2011 Super-elastic graphene ripples for flexible strain sensors ACS Nano 5 3645–50

[24] Androulidakis C, Koukaras E N, Pastore Carbone M G, Hadjinicolau M and Galiotis C 2017 Wrinkling formation in simply-supported graphene under tension and compression loadings Nanoscale 9 18180–8

[25] Androulidakis C, Koukaras E N, Rahova J, Sampaikumar K, Parthenios J, Papgelis K, Frank O and Galiotis C 2017 Wrinkled few-layer graphene as highly efficient load bearer ACS Appl. Mater. Interfaces 9 26593–601

[26] Li L, Reich S and Robertson J 2005 Defect energies of graphite: density-functional calculations Phys. Rev. B 72 184109

[27] Cortijo A and Vozmediano M A H 2007 Electronic properties of curved graphene sheets Europhys. Lett. 77 47002

[28] Ariza M P and Ortiz M 2010 Discrete dislocations in graphene J. Mech. Phys. Solids 58 710–34

[29] Duplock E J, Scheffler M and Lindan P J D 2004 Hallmark of perfect graphene Phys. Rev. Lett. 92 225502

[30] Lherbier A, Blase X, Niquet Y-M, Triozon F and Roche S 2008 Charge transport in chemically doped 2D graphene Phys. Rev. Lett. 101 036808

[31] Han J, Pugno N M and Ryu S 2015 Nanoindentation cannot accurately predict the tensile strength of graphene or other 2D materials Nanoscale 7 15672–9

[32] Jiang T, Huang R and Zhu Y 2014 Interfacial sliding and buckling of monolayer graphene on a stretchable substrate Adv. Funct. Mater. 24 396–402

[33] Bonsgjeest M S, Bendia N, Mathur S, Kimouche A, Johnson H T, Coraux J and Pochet P 2015 Strain relaxation in CVD graphene: wrinkling with shear lag Nano Lett. 15 5098–104

[34] Li Z, Kinloch I A, Young R J, Novoselov K S, Anagnostopoulos G, Parthenios J, Galiotis C, Papgelis K, Lu C-Y and Brittnell L 2015 Deformation of wrinkled graphene ACS Nano 9 3917–25

[35] Vasić B, Zurutuza A and Gajić R 2016 Spatial variation of wear and electrical properties across wrinkles in chemical vapour deposition graphene Carbon 102 304–10

[36] Tong Y, Bohm S and Song M 2013 Graphene-based materials and their composites as coatings Austin J. Nanomed. Nanotechnol. 1 1003

[37] Raju A P A, Lewis A, Derby B, Young R J, Kinloch I A, Zan R and Novoselov K S 2014 Wide-area strain sensors based upon graphene-polymer composite coatings probed by Ramanscopicy Adv. Funct. Mater. 24 2865–74

[38] Won S, Hwangbo Y, Lee S-K, Kim K-S, Lee S-M, Lee H-J, Ahn J-H, Kim J-H and Lee S-B 2014 Double-layer CVD graphene as stretchable transparent electrodes Nanoscale 6 6057–64

[39] Lee Y, Bae S, Jung H, Jung S, Zhu S-E, Sim S H, Song Y I, Hong B H and Ahn J-H 2010 Wafer-scale synthesis and transfer of graphene films Nano Lett. 10 490–3

[40] Kim Y-J, Cha J Y, Ham H, Huh H, So D-S and Kang I 2011 Preparation of piezoresistive nano smart hybrid material based on graphene Curr. Appl. Phys. 11 S350–2

[41] Bonacorso F, Sun Z, Hasan T and Ferrari A C 2010 Graphene photonics and optoelectronics Nat. Photon. 4 611–22

[42] Kim K S, Zhao Y, Jung H, Lee S Y, Kim J M, Kim K S, Ahn J-H, Kim P, Choi J-Y and Hong B H 2009 Large-scale pattern growth of graphene films for stretchable transparent electrodes Nature 457 706–10

[43] Kim B J, Jiang H, Lee S-K, Hong B H, Ahn J-H and Cho J H 2010 High-performance flexible graphene field effect transistors with ion gel gate dielectrics Nano Lett. 10 5464–6

[44] Schrier J 2010 Helium separation using porous graphene membranes J. Phys. Chem. Lett. 1 2284–7

[45] Banhart F, Kotakoski J and Krasheninnikov A V 2010 Structural defects in graphene ACS Nano 5 26–41

[46] Berger D and Ratsch C 2016 Line defects in graphene: how doping affects the electronic and mechanical properties Phys. Rev. B 93 235441

[47] Škákalová V and Kaiser A B 2014 Graphene: Properties, Preparation, Characterisation and Devices (Amsterdam: Elsevier)

[48] Hu K, Kulkarni D D, Choi I and Tsukruk V V 2014 Graphene-polymer nanocomposites for structural and functional applications Prog. Polym. Sci. 39 1934–72

[49] Mital G, Dhand V, Rhee K Y, Park S-J and Lee W R 2015 A review on carbon nanotubes and graphene as fillers in reinforced polymer nanocomposites J. Ind. Eng. Chem. 21 11–25

[50] Terrones M, Martín O, González M, Pozuelo J, Serrano B, Cabanelas J C, Vega-Diaz S M and Baselga J 2011 Interphases in graphene polymer-based nanocomposites: achievements and challenges Adv. Mater. 23 5302–10
[51] Murakami K, Kadokawa T and Fujita J-I 2013 Damage and strain in single-layer graphene induced by very-low-energy electron-beam irradiation Appl. Phys. Lett. 102 043111

[52] Imamura G and Saiki K 2013 UV-irradiation induced defect formation on graphene on metals Chem. Phys. Lett. 587 56–60

[53] Lucchese M M, Stavale F, Ferreira E H M, Vilani C, Moutinho M V O, Capaz R B, Achete C A and Jorio A 2010 Quantifying ion-induced defects and Raman relaxation length in graphene Carbon 48 1592–7

[54] Cançado L G, Jorio A, Ferreira E H M, Stavale F, Achete C A, Capaz R B, Moutinho M V O, Lombardo A, Kulmala T S and Ferrari A C 2011 Quantifying defects in graphene via Raman spectroscopy at different excitation energies Nano Lett. 11 3190–6

[55] Eckmann A, Felten A, Mishchenko A, Britnell L, Krupke R, Novoselov K S and Casiraghi C 2012 Probing the nature of defects in graphene by Raman spectroscopy Nano Lett. 12 3926–30

[56] Kim B H et al 2012 N-type graphene induced by dissociative H2 adsorption at room temperature Sci. Rep. 2 690

[57] Allouche A and Ferro Y 2006 Dissociative adsorption of small molecules at vacancies on the graphite (0 0 0 1) surface Carbon 44 3320–7

[58] Diño W A, Miura Y, Nakamishi H, Kasai H, Sugimoto T and Kondo T 2004 H2 dissociative adsorption at the armchair edges of graphite Solid State Commun. 132 713–8

[59] Anagnostopoulos G, Androulidakis C, Koukaras E N, Tsoukleri G, Polyzos I, Parthenios J, Papagelis K and Galiotis C 2011 Quantifying defects in graphene with atomic force microscopy with a microsphere tip Nanoscale 7 10760–6

[60] Moutinho M V O, Capaz R B, Achete C A, Jorio A, Reina A and Kong J 2012 Graphene growth by CVD methods Nano Lett. 12 6904–10

[61] Yu T 2010 Modulating the electronic structures of graphene in chemical vapor deposition Nano Lett. 10 5176–81

[62] Yu D, Shi J and Lu J 2013 Interfacial properties of bilayer graphene on metal substrates Appl. Phys. Lett. 103 173104

[63] Ilie A, Hart A, Flewitt A J, Robertson J and Milne W I 2000 Effect of work function and surface microstructure on field emission of tetrahedral amorphous carbon J. Appl. Phys. 88 6002–10

[64] Ferrari A C and Basko D M 2013 Raman spectroscopy as a versatile tool for studying the properties of graphene Nat. Nanotechnol. 8 235–46

[65] Liu N, Pan Z, Fu L, Zhang C, Dai B and Liu Z 2011 The origin of wrinkles on transferred graphene Nano Res. 4 996–1004

[66] Li Y and Chopra N 2014 Progress in large-scale production of graphene: II. Vapor methods JOM 67 44–52

[67] Chen P Y, Sudhi J, Qiu Y, Valentin T M, Steinberg R S, Wang Z, Hurt R H and Wong I Y 2016 Multiscale graphene topographies programmed by sequential mechanical deformation Adv. Mater. 28 3564–71

[68] Jiang T and Zhu Y 2015 Measuring graphene adhesion using atomic force microscopy with a microsphere tip Nanoscale 7 10760–6

[69] Reina A and Kong J 2012 Graphene growth by CVD methods Adv. Mater. 24 5989–5002

[70] Shin Y J, Wang Y, Huang H, Kalon G, Wei A T S, Shen Z, Bhatia C S and Yang H 2010 Surface-energy engineering of graphene Langmuir 26 3798–802

[71] Kozbial A, Li Z, Conaway C, McKinley R, Dhingra S, Vahdat V, Zhou F, D’Urso B, Liu H and Li L 2014 Study on the surface energy of graphene by contact angle measurements Langmuir 30 8598–606

[72] Malard L M, Pimenta M A, Dresselhaus G and Dresselhaus M S 2009 Raman spectroscopy in graphene Phys. Rev. B 79 153401

[73] Dresselhaus M S, Jorio A, Hofmann M, Dresselhaus G and Saito R 2010 Perspectives on carbon nanotubes and graphene Raman spectroscopy Nano Lett. 10 751–8

[74] Vahdat V, Zhou F, D’Urso B, Liu H and Li L 2014 Study on the surface energy of graphene by contact angle measurements Langmuir 30 8598–606

[75] Androulidakis C, Koukaras E N, Parthenios J, Kalosakas G, Papagelis K and Galiotis C 2015 Graphene flakes under controlled biaxial deformation Sci. Rep. 5 18219

[76] Frank O, Vejpichvratova J, Holy V, Kavan L and Kalbac M 2014 Interaction between graphene and copper substrate: the role of lattice orientation Carbon 68 440–51

[77] Wood J D, Schmucker S W, Lyons A S, Pop E and Lyding J W 2011 Effects of polycrystalline Cu substrate on graphene growth by chemical vapor deposition Nano Lett. 11 4547–54

[78] Ferrari A C and Basko D M 2013 (REVIEW) Raman spectroscopy as a versatile tool for studying the properties of graphene Nat. Nanotechnol. 8 235–46

[79] Reina A and Kong J 2012 Graphene growth by CVD methods Nano Lett. 12 2408–13

[80] Yu Q et al 2011 Control and characterization of individual grains and grain boundaries in graphene grown by chemical vapour deposition Nat. Mater. 10 443–9

[81] Reina A and Kong J 2012 Graphene growth by CVD methods Graphene Nanoelectronics: From Materials to Circuits ed R Murali (Boston, MA: Springer) pp 167–203

[82] Kalbac M, Frank O and Kavan L 2012 The control of graphene double-layer formation in copper-catalyzed chemical vapor deposition Carbon 50 3682–7

[83] Cabrini A, Busetto M, Alboni M and Marconato G 2012 Control of graphene growth by CVD methods Nano Lett. 12 2408–13

[84] Yu Q et al 2011 Control and characterization of individual grains and grain boundaries in graphene grown by chemical vapour deposition Nat. Mater. 10 443–9

[85] Reina A and Kong J 2012 Graphene growth by CVD methods Graphene Nanoelectronics: From Materials to Circuits ed R Murali (Boston, MA: Springer) pp 167–203

[86] Kalbac M, Frank O and Kavan L 2012 The control of graphene double-layer formation in copper-catalyzed chemical vapor deposition Carbon 50 3682–7

[87] Cabrini A, Busetto M, Alboni M and Marconato G 2012 Control of graphene growth by CVD methods Nano Lett. 12 2408–13

[88] Yu Q et al 2011 Control and characterization of individual grains and grain boundaries in graphene grown by chemical vapour deposition Nat. Mater. 10 443–9
[90] Kalbac M, Kong J and Dresselhaus M S 2012 Raman spectroscopy as a tool to address individual graphene layers in few-layer graphene J. Phys. Chem. C 116 19046–50

[91] Martins Ferreira E H, Moutinho M V O, Stavale F, Lucchese M M, Capaz R B, Achete C A and Jorio A 2010 Evolution of the Raman spectra from single-, few-, and many-layer graphene with increasing disorder Phys. Rev. B 82 125429

[92] Das A, Chakraborty B and Sood A K 2008 Raman spectroscopy of graphene on different substrates and influence of defects Bull. Mater. Sci. 31 579–84

[93] Casiraghi C 2009 Probing disorder and charged impurities in graphene by Raman spectroscopy Phys. Status Solidi 3 175–7

[94] Ryan B, Luiz Gustavo C and Lukas N 2015 Raman characterization of defects and dopants in graphene J. Phys.: Condens. Matter 27 083002

[95] López-Polín G, Gómez-Navarro C, Parente V, Guinea F, Katsnelson M I, Pérez-Murano F and Gómez-Herrero J 2015 Increasing the elastic modulus of graphene by controlled defect creation Nat. Phys. 11 26–31

[96] Papageorgiou D G, Kinloch I A and Young R J 2017 Mechanical properties of graphene and graphene-based nanocomposites Prog. Mater. Sci. 90 75–127

[97] Mohiuddin T M G et al 2009 Uniaxial strain in graphene by Raman spectroscopy: G peak splitting, Gruneisen parameters, and sample orientation Phys. Rev. B 79 205433

[98] Tsoukleri G, Parthenios J, Papagelis K, Jalil R, Ferrari A C, Geim A K, Novoselov K S and Galiotis C 2009 Subjecting a graphene monolayer to tension and compression Small 5 2397–402

[99] Tsoukleri G, Parthenios J, Galiotis C and Papagelis K 2015 Embedded trilayer graphene flakes under tensile and compressive loading 2D Mater. 2 024009

[100] Bousa M et al 2016 Stress and charge transfer in uniaxially strained CVD graphene Phys. Status Solidi b 253 2355–61

[101] Wang G, Dai Z, Liu L, Hu H, Dai Q and Zhang Z 2016 Tuning the interfacial mechanical behaviors of monolayer graphene/PMMA nanocomposites ACS Appl. Mater. Interfaces 8 22554–62

[102] Frank O et al 2011 Raman 2D-band splitting in graphene: theory and experiment ACS Nano 5 2231–9

[103] Huang M, Yan H, Heinz T F and Hone J 2010 Probing strain-induced electronic structure change in graphene by Raman spectroscopy Nano Lett. 10 4074–9

[104] Zhang R, Ning Z, Zhang Y, Zheng Q, Chen Q, Xie H, Zhang Q, Qian W and Wei F 2013 Superlubricity in centimetres-long double-walled carbon nanotubes under ambient conditions Nat. Nanotechnol. 8 912–6

[105] Wang G, Liu L, Dai Z, Liu Q, Miao H and Zhang Z 2015 Biaxial compressive behavior of embedded monolayer graphene inside flexible poly (methyl methacrylate) matrix Carbon 86 69–77