Controlling and Monitoring Crack Propagation in Monolayer Graphene Single Crystals

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The evolution and propagation of cracks in exfoliated monolayer graphene single crystals and their associated stress fields are studied using Raman spectroscopy as a strain sensor. Such stress fields are found to extend over several microns, and their analysis leads to the fracture behavior of graphene being interpreted using linear elastic fracture mechanics. It is shown that propagation of a sharp crack occurs at a critical stress intensity factor $K_c = 4.0$ MPa m$^{1/2}$, similar to the earlier findings of theoretical simulations. In contrast, a blunt crack lying along an irrational direction of the crystal is found to have a less localized stress field at the crack tip and propagate at a value of $K_c > 9$ MPa m$^{1/2}$. It is also shown that once crack propagation takes place, the cracks rotate to become aligned approximately perpendicular to the tensile axis, regardless of the crystallographic orientation of the graphene. Based upon this, a simple strain engineering method is proposed to control the propagation of cracks. This has important implications for the use of graphene in practical applications and suggests a simple method to control the formation of cracks in graphene through the application of strain.

1. Introduction

Graphene, as a one-atom thick 2D material,[1–3] has been playing an increasingly important role in fields such as nanocomposites and flexible electronics, in applications that exploit its exceptional mechanical, electronic, thermal, and barrier properties.[4,5]

In particular, its nanostructure and 2D geometry enable it to be an excellent candidate for sensing applications. A graphene-based composite strain sensor with graphene sheets dispersed in a viscoelastic polymer has been demonstrated to be able to sense the average strain with high sensitivity.[6] Sensing localized strain is also possible, as recently demonstrated by Liu et al.[7] whereby a strain sensor consisting of monolayer graphene in combination with Raman spectroscopy is shown to be capable of sensing the stress fields around fine defects in a polymer as small as $\approx 100$ nm. However, as a 2D material of atomic thickness, graphene inevitably wrinkles and cracks,[8–11] which leads to a strength of $\approx 10$ GPa, much weaker than the ideal value of $\approx 130$ GPa for perfect graphene,[12] due to the presence of defects.[13]

Cracks in graphene have high stress concentrations in the vicinity of the crack tip, leading to deformation over a region much larger than the crack itself. This is of particular importance for applications such as in sensors and devices. If fine features are to be sensed with high spatial resolution in nanodevices, the presence of the cracks damages the structural integrity of graphene and the stress concentration interferes with the sensing of small features on the target. This is even more important for other types of strain sensors, such as where cracks are generated artificially through crack engineering[14,15] or for kirigami structures,[16] based on the mechanisms of electrical disconnection and reconnection of crack surfaces upon deformation, that give ultrahigh strain sensitivity with bespoke flexibility.[7,16,17] The mechanics and control of crack propagation in graphene and the complex stress field at the crack tip have, however, not been widely studied. Understanding these will not only solve the issues mentioned above, but also give insight into the further control of the fracture of graphene. One application could be in the fabrication of nanoribbons, as demonstrated recently by Chen et al.[18] who made use of the localized strain in a necked polymer to precisely cut graphene into nanoribbons.

The majority of work that has been carried out in order to understand the fracture of graphene has used simulations.[19–26] The reason for this may be because its relatively simple structure makes it particularly amenable to theoretical analysis. Some 25 years ago, even before graphene was first isolated,[19] Omelchenko et al.[24] used molecular dynamics to study crack propagation and fracture in a “graphite sheet” and reported a value of the critical stress intensity factor $K_c$. 

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of 4.7 MPa m$^{1/2}$ from the Griffith analysis.\cite{27} It was found\cite{19} from simulation of the stress field around a crack tip that the Griffith criterion applies to cracks larger than 10 nm in graphene, and that the cracks propagate preferentially along with the graphene zigzag direction. The majority of the simulation work is, however, limited to a scale of up to hundreds of atoms. Although the effect of defects such as cracks and grain boundaries can be simulated at the atomic level, such simulations are is still not completely satisfactory for applications on a larger scale.

Compared to simulations, fewer experimental fracture studies have been undertaken because of the catastrophic failure of graphene and difficulties in applying strain to specimens with small dimensions.\cite{22,28–31} In situ microscopy techniques have mainly been used as summarized in the recent review by Li et al.\cite{32} The main approaches employed include direct measurement using AFM\cite{28,33,34} or imaging techniques\cite{22,35} such as SEM/TEM.\cite{28,36} Such techniques typically record stress-strain curves under different forms of deformation, and follow the fracture mechanics from the dependence of the fracture stress upon the length of preformed cracks. This was done originally for graphene and, then more recently, for other 2D materials such as multilayer functionalized graphene\cite{31} and hBN.\cite{37} These approaches are, however, not able to monitor the stress fields around cracks unlike numerous studies that have been undertaken upon engineering materials using techniques such as synchrotron X-ray diffraction\cite{38} or neutron scattering.\cite{39} The spatial resolutions of X-ray diffraction and neutron scattering are, however, typically much larger than that required for the analysis of the stress field around a crack in nanomaterials.\cite{38} A recent study\cite{40} attempted to reveal the stress field around a crack in polycrystalline CVD graphene deformed on a PDMS substrate using Raman spectroscopy. The authors noted that the stress field they found was anomalous in that a stress concentration at some distance ahead of the crack tip is quite different from the typical patterns predicted by the Griffith theory.\cite{19,31} In addition, several studies have reported strategies for generating cracks artificially for applications such as ultrasensitive strain sensing,\cite{27} obtaining selective edge geometries,\cite{41} and generating high flexibility.\cite{38} The fundamental mechanisms have, however, been investigated predominately using simulations and not have been explained experimentally, particularly for single-crystal graphene flakes.

In this present investigation, Raman spectroscopy has been employed as a technique to monitor the evolution and propagation of natural cracks in graphene and visualize the development of their associated strain fields. This has enabled the fracture behavior of cracks in graphene to be analyzed using linear elastic fracture mechanics without the need to either accurately measure the crack length or monitor the crack tip geometry, and furthermore, allow characterization of the nature of small and even invisible cracks. This can be contrasted with previous studies that measured the stress required to propagate a crack of known length\cite{22,31} or reported the strain fields only around static cracks.\cite{40} The underlying interplay between the crystallography of the graphene and strain direction has also been revealed, based on which, a strain engineering method has been proposed to control the direction of propagation of cracks in graphene.

2. Results and Discussion

2.1. Raman Mapping

The deformation of the graphene on PMMA substrates was followed by strain mapping using Raman spectroscopy. Figure 1a
shows the Raman spectrum of the PMMA substrate and that of an exfoliated graphene monolayer on the substrate. The characteristic Raman bands of PMMA can be seen along with the G band (≈1585 cm$^{-1}$) and 2D band (≈2696 cm$^{-1}$) for the specimen with a graphene single crystal on its top surface. The intensity of the graphene 2D band is more than twice that of the G band which confirms that this is monolayer graphene.[42] Additionally, there is no Raman D band, normally observed at around 1350 cm$^{-1}$ in graphene which indicates that the graphene is relatively defect free.[43] Another interesting feature of Figure 1a is that the Raman bands for the graphene are of similar intensity to those of the PMMA beam, even though the graphene monolayer is only 0.34 nm thick. This is a vivid demonstration of the strong resonant enhancement of the Raman scattering from the graphene reflecting its unique electronic structure.[44]

It is well established that upon the deformation of graphene, phonon softening occurs in tension with the Raman 2D band undergoing a redshift as shown in Figure 1b.[45,46] As demonstrated, the shift rate of the 2D band position ($\omega_{2D}$) is approximately –60 cm$^{-1}$/% strain for monolayer graphene, both determined experimentally and also calculated using knowledge of the Gruneisen parameter.[45–48] This reference value was used as a universal calibration where the experimentally obtained $\omega_{2D}$ can be converted to the level of strain in graphene, in order to map the strain distributions in the monolayer graphene deformed on the PMMA substrate (Figure 1c). This approach was employed a number of years ago to monitor strain over a wide area in graphene,[16] but was shown recently to also be capable of sensing fine defects in a polymer substrate, beyond the resolution of Raman spectroscopy (≈1 µm), based upon the stress field around the defects.[5] Herein, the application of this method is demonstrated further by using Raman spectroscopy to monitor the evolution of fine, barely visible cracks in graphene and analyzing the mechanics of their propagation.

### 2.2. Sharp Crack

#### 2.2.1. Strain Distribution

Figure 2a shows an optical micrograph of fragments of an exfoliated graphene flake on the surface of a PMMA beam. It was confirmed that the flake was of monolayer graphene as the ratio of the intensity of the 2D band to that of the G band, $I_{2D}/I_G$ was greater than unity (c.f. Figure 1a). Even though such a flake is only one atom thick, it is known that 2.3% of the light is absorbed[49] which renders the graphene visible under the optical microscope.[50] The left-hand fragment of the flake was first studied, initially by low-resolution Raman mapping using a step size of 1 µm. Figure 2b shows the Raman map of this flake fragment before it was subjected to deformation. Polarized Raman spectroscopy was used to determine the crystallographic orientation of this flake, as indicated by the hexagons in Figure 2b, from the splitting of the G band during deformation (Figure 2c and Supporting Information). It was confirmed that the zigzag direction of the flake was approximately horizontal. A Raman map of the highlighted region of the flake is shown in Figure 2d showing that there were low levels of residual strain in the flake, probably induced during the deposition process. A pre-existing edge crack, formed during the exfoliation process, can be visualized at the bottom of the flake from the absence of residual stress and a comparison with Figure 2b shows that this pre-existing crack was aligned along the armchair direction of the graphene crystal.

The flake was subjected to deformation by bending the PMMA beam and Figure 2e shows a low-resolution Raman image of the bottom region of the flake at 0.41% strain following propagation of the crack. It can be seen that the pre-existing crack propagated along the original armchair direction and then changed direction by 30° to become perpendicular...
to the direction of applied strain and so parallel to the zig-zag direction of the graphene crystal.

High-resolution Raman mapping, using a step size of 0.5 μm, was also undertaken in the region of the crack marked by the red rectangle in Figure 2d during the deformation of the crystal as shown in Figure 3. Figure 3a–d shows the strain distributions and the stress fields in the vicinity of the crack tip for overall strains of 0.12%, 0.25%, 0.33%, and 0.41%, respectively. It can be seen that there is no stress transfer across the crack as it does not bear any load. Hence a significant strain gradient can be found each side of the crack, particularly at high strain levels, due to interfacial stress transfer through a shear-lag process. A stress concentration also develops ahead of the crack tip and the crack eventually propagates at a strain of between 0.33% and 0.41%, changing direction by 30° to become perpendicular to the direction of applied stress (vertical). To our knowledge, this is the first time that the propagation of a crack in graphene as strain is increased and its associated stress field have been captured experimentally. The propagation direction and the morphology of the crack in the graphene can be confirmed using AFM as shown in Figure S3 in the Supporting Information. The interfacial interaction between the PMMA substrate and graphene stabilizes crack propagation so that it can be controlled and monitored. The failure strain of the graphene monolayer flake and the angle α was 60°. The reduction in the strength of materials due to the presence of flaws and defects was recognized many years ago by Griffith, and the large body of subsequent experimental and theoretical work upon the phenomenon is now termed “Fracture Mechanics.” The stress field and stress concentration further enable the fracture mechanics of the crack in graphene to be analyzed. The stress field around a sharp crack in a linear elastic material can be uniquely defined by a parameter known as the stress intensity factor, K, and fracture occur when the stress intensity factor reaches a critical value, Kc. Hence K is a stress field parameter independent of the material whereas Kc, being a measure of the fracture toughness, is a material property.

Most of the analyses upon fracture mechanics have dealt with cracks aligned at 90° to the direction of the tensile stress, σ, but the initial crack in Figure 3 is inclined at 60° to the tensile axis (vertical). The analysis of the stress field around a crack of length 2a inclined at an angle θ to the tensile axis, as shown in the schematic diagram in Figure 3e, has fortunately been undertaken for an elastic material by Efis and Subramonian. They showed that the stress components as a function of r, the distance from the crack tip, in the vicinity of the crack tip (0 < r/a < 1) are given by

\[ \sigma_x = \frac{K_I}{\sqrt{2\pi r}} \cos \theta \left( 1 - \sin \frac{\theta}{2} \sin \frac{3\theta}{2} \right) - \frac{K_{II}}{\sqrt{2\pi r}} \sin \frac{\theta}{2} \cos \frac{\theta}{2} \cos \frac{3\theta}{2} \]  (2)

\[ \sigma_y = \frac{K_I}{\sqrt{2\pi r}} \sin \frac{\theta}{2} \cos \frac{\theta}{2} \cos \frac{3\theta}{2} + \frac{K_{II}}{\sqrt{2\pi r}} \cos \frac{\theta}{2} \left( 1 - \sin \frac{\theta}{2} \sin \frac{3\theta}{2} \right) \]  (3)

where \( K_I \) and \( K_{II} \) are the mode I and mode II stress intensity factors, and \( \theta \) is the angle between r and the crack plane. It is now possible to compare the strain distributions in Figure 3a–d measured in the vicinity of the crack with the theoretical ones given by the above equations hence determining the stress intensity factors.

It was assumed that \( \epsilon_{yy} = \epsilon \sin \theta \) where \( \epsilon \) is the axial tensile strain determined from the Raman band shifts (Figure 1c). In this case, the crack was aligned initially along the armchair direction of the graphene monolayer flake and the angle \( \alpha \) was 60°. The dependence of \( \epsilon_{yy} \) upon \( r \) for a given value of \( \theta \) was determined by interpolation of the 0.5 μm square arrays of strain data used in the Raman strain maps using the Origin graphing and analysis package (Originlab Corporation). Figure 3f shows the measured variation of \( \epsilon_{yy} \) as a function of distance from the crack tip, \( r \) for \( \theta = 0 \) (i.e., in the plane of the crack). When \( \theta = 0 \) Equation (1) can be simplified to give \( \sigma_{yy} = \frac{K_I}{\sqrt{2\pi r}} \) and the theoretical variation of \( \epsilon_{yy} = \sigma_{yy}/E\_\text{g} \) where \( E\_\text{g} \) is the Young’s modulus of the graphene, 1050 GPa) with \( r \) is also given in Figure 3f. It can be seen that the experimental data points generally lie above the theoretical curve but the curves converge as \( r \rightarrow 0 \). An alternative way to analyze the stress field is to plot \( \sigma_{yy} \sqrt{2\pi r} \) as a function of \( r \) as shown in Figure 3g for the different levels of applied strain. The value of stress intensity factor \( K \) at each strain level can then be simply determined by extrapolating the data points (fitted in Origin to a third order polynomial function) to the intercept at \( r = 0 \). Figure 3h shows the dependence of \( \epsilon_{yy} \) upon \( r \) and the vertical dashed line indicates the strain level by which crack propagation had occurred. The linear dependence of \( K \) upon the applied strain is strong confirmation of the applicability of linear elastic fracture mechanics to crack propagation in this one-atom thick graphene crystal on the microscale. Since crack propagation was found to take place at a strain level of between 0.33% and 0.41% the value of \( K_c \) is estimated to be 4.0 ± 0.4 MPa m^{1/2}. It was shown in Figure 2 that the crack initially propagated in the armchair direction of the crystal and this value of \( K_c \) is very similar to the values calculated theoretically for armchair direction cracks confirming that in this case, we are dealing with a relatively sharp crack. It also corresponds to a critical strain energy release rate G of around 16 J m^{-2} confirming the brittle nature of the material.

It is important to point out that the value of \( K_c \) was determined solely from the strain distribution in the strain field ahead of the crack tip which is unaffected by the complex state of stress behind the crack tip. It is quite different from methods used previously that rely upon measuring the fracture stress from a stress-strain curve and the length of a pre-fractured crack, that are not able to reveal the stress field and the stress concentration ahead of the crack tip. X-ray diffraction and neutron scattering have spatial resolution typically in
the order of 1 mm in diameter leading to much lower resolution analysis of the stress field around a crack. \[38\] In contrast, the spatial resolution of Raman spectroscopy $\approx 1$ $\mu$m spot size (with only $\approx 38 \times 10^6$ atoms $\mu$m$^{-2}$ in the laser spot) enables the submicron mapping of the stress/strain field in the monolayer graphene. Another advantage of the technique is that it

Figure 3. The measured strain distribution around the crack at a) 0.12%, b) 0.25%, c) 0.33%, and d) 0.41% applied strain. e) Schematic illustration of the pre-crack along the armchair direction and the associated definitions of $r$ and $\theta$. f) Measured and theoretical variation of strain $\epsilon_y$ as the function of $r$ at different applied strain levels. The error bars indicate the precision of knowing the position of the laser beam relatively to the crack tip. g) Variation of $\sigma_y \sqrt{2\pi r}$ as a function of $r$ at different applied strain levels. The vertical dashed line corresponds to a strain of 0.41% following crack propagation.
can also be used for microstructural analysis of the graphene, in particular being able to determine the crystallographic orientation of single crystals. One challenge in crack tip stress analysis is knowing the exact position of the crack tip.\[38\] In our study, this could only be done to a precision of the order of ±0.25 μm and this is the main limitation upon the accuracy of the determination of parameters such as $K_c$. With this resolution,\[39\] it is not possible to capture non-linear processes that may occur close to the crack tip but further improvement might be possible using Raman spectroscopy with a higher spatial resolution.

2.3. Blunt Crack

2.3.1. Strain Distribution

Figure 4a shows the optical micrograph of a different exfoliated graphene monolayer flake that was subjected to deformation. A low resolution, 1 μm step Raman map of the flake at 0% strain is shown in Figure 4b showing some local variation of strain as the result of the deposition process. Figure 4c shows that when the strain is increased to 0.25% the overall level of strain in the flake increases and eventually the flake fractures into different fragments at 0.37% strain (Figure 4d). Polarized Raman was again used to determine the crystallographic orientation of the flake, as indicated by the hexagons in Figure 4b, from splitting of the G band during deformation (Figure 4c and Supporting Information). Careful examination of the fragmented flake in Figure 4d shows that it contains two cracks, one across whole flake going through its center and another above it terminating in the middle of the flake. We then undertook an investigation into why the crack that had terminated in the middle of the flake had propagated in this way and the effect of reloading the flake.

High-resolution Raman mapping, using a step size of 0.5 μm, was undertaken on reloading the flake shown in Figure 4. This is presented in Figure 5 where Raman strain maps are shown in the vicinity of the stationary crack, indicated by the red rectangle in Figure 4d, at different levels of applied strain. The behavior is similar to that seen in Figure 3 where the overall strain in the flake builds up as the strain is increased (Figure 5a–c) until propagation takes place by a strain of 0.44% (Figure 5d). A broad region of strain concentration develops at the crack tip during loading and there is again no stress transfer across the crack plane. The crack is aligned initially at an angle of $\alpha \approx 73^\circ$ to the tensile axis (vertical) and the direction of crack propagation changes during growth until it becomes approximately $90^\circ$ to the tensile axis (Figure 5d). A schematic diagram of the crack in the flake is shown in Figure 5e and since the zigzag direction is $\approx 5^\circ$ (Figure 4e) to the vertical it means that in this case the crack is aligned initially between the zigzag and armchair directions.

2.3.2. Fracture Mechanics

The fracture mechanics analysis was undertaken in a similar way to that described in Section 2.2.2 apart from the fact that the crack was aligned initially along an irrational direction of the graphene monolayer flake at an $\alpha$ of $\approx 73^\circ$ to the tensile axis (Figure 5e). Figure 5f shows the measured and theoretical (determined using Equation (1)) variation of $\varepsilon_{tt}$ as a function of $\theta$ for $\theta = 0$ (i.e., in the plane of the original crack). The plot of $\sigma_{yy} \sqrt{2\pi r}$ as a function of $r$ is shown in Figure 5g for the different levels of applied strain. Figure 5h shows the dependence of $K$ upon applied strain and there is again an approximately linear dependence of $K$ upon the level of applied strain. Since crack propagation occurs at a strain level of between 0.40% and 0.44% the value of $K_c$ is estimated to
be 9.2 ± 0.8 MPa m$^{1/2}$. In contrast to the sharp crack in the graphene flake shown earlier, the crack shown in Figure 5 appears to be a blunt one.

It is of interest to speculate why $K_c$ is considerably higher for the crack in Figure 5 than it is for the armchair direction crack in Figure 3. One possibility is that the Figure 5 crack is...
lying between the zigzag and armchair directions and so not aligned along a crystallographic direction. The theoretical simulations discussed earlier\[23,25]\ show that the difference in $K_c$ between cracks propagating in the two crystallographic directions, armchair and zigzag is small and so it is unlikely that the exact direction of propagation will make much difference to $K_c$. Figure 4 shows that this crack did not propagate fully across the crystal on the first loading implying that it may have been branched\[24]\ or kinked,\[54]\ or had been impeded by a defect or hole. It is impossible with the resolution of our Raman mapping technique to know the exact reason for this different behavior. What is clear, however, is that the contours in the Raman strain maps in Figure 5 show that there was a less-localized stress concentration for this blunt crack leading to the considerably higher value of $K_c$ for propagation, compared to the value determined for the sharp crack shown in Figures 2 and 3.

These observations relate mainly to the continuum regime, where sub-micrometer scale Raman measurements have been used to interpret mechanical behavior using continuum mechanics theory. They have implications for the use of graphene in applications such as composites, devices, and strain sensors. It has been revealed that a large area, of the order of several microns in dimensions, can be affected by the stress field of the crack potentially leading to, for example, a modification of the electronic properties such as bandgap and carrier mobility in the affected areas.\[55]\ This is of vital importance to applications where cracks are created artificially on graphene for stretchability and strain sensitivity in nanodevices.\[4,7,14–16\]

2.4. Direction of Crack Propagation

The monitoring of crack propagation described above has also fundamentally rationalized the method to control the crack propagation in graphene simply by the application of strain. The propagation of cracks in graphene has been found to take place preferentially along zigzag direction, with a slightly lower fracture energy than that in the armchair direction.\[19]\ This explains why the majority of the cracks formed in CVD growth\[41]\ and during liquid-phase exfoliation\[56]\ lie naturally along the zigzag direction. We have summarized our findings in Figure 6a where the geometries of six cracks in five different graphene monolayer single-crystal flakes have been analyzed following tensile deformation (vertical). It can be seen that the cracks become aligned approximately perpendicular to the direction of the tensile axis with $\alpha = 90^\circ$, regardless of the crystallographic orientation of the flake (as indicated by the corresponding hexagons in Figure 6d–h). Even cracks that were initially aligned at an inclined angle to the tensile axis, change their propagation direction to become aligned approximately perpendicular to the tensile axis (Figures 3d and 5d and the open circles in Figure 6a), due to the asymmetrical stress field ahead of the crack tip.\[57]\ This confirms that although $K_c$...
might be slightly different for crack propagation in different crystallographic directions, the direction of crack propagation can still be effectively controlled by the direction of application of strain.\(^3^{[9]}\) It also explains why the localized strain induced by defects or grain boundaries, could be one of the reasons why microscopically smooth graphene edges can have local atomic-scale roughness with different types of edges. This phenomenon is clearly seen in the high-resolution TEM analysis of a zigzag crack from the edge of an exfoliated monolayer flake (Figure 6b) drawn schematically in Figure 6c, and shown previously in CVD grown graphene.\(^4^{[1]}\) In summary, we have shown that it is possible to control and manipulate the direction of crack propagation in graphene, and possibly other 2D materials, through engineering the substrate.\(^7^{[18]}\)

3. Conclusions

We have demonstrated that is possible to control and monitor the propagation of the cracks in monolayer graphene single crystals and that Raman spectroscopy can be used for the mapping of the stress field in the vicinity of crack tips. The stress field has enabled the fracture behavior of invisible cracks in graphene to be analyzed, where graphene behaves as an ideal brittle material with a critical stress intensity factor of \(K_c = 4.0 \pm 0.4 \text{ MPa m}^{1/2}\). In addition, it has been found that once crack propagation occurs, the cracks grow preferentially in a direction perpendicular to the tensile axis, regardless of the crystallographic orientation of the graphene crystal. This has fundamentally rationalized a proposed strain engineering method to control the crack propagation in graphene simply by the application of strain. These findings will be important for the fabrication of graphene strain sensors and other devices where the ability to cleave graphene accurately into thin strips is of particular importance.

It is clear that the Raman mapping technique may also be applicable to a broad range of nanomaterials. For example, monolayers of 2D transition metal dichalcogenides (TMDs) such as tungsten disulfide, WS\(_2\) have well-defined Raman monolayers of 2D transition metal dichalcogenides (TMDs) applicable to a broad range of nanomaterials. For example, where the ability to cleave graphene accurately into thin strips by the application of strain. These findings will be important method to control the crack propagation in graphene simply in CVD grown graphene.\(^4^{[1]}\) In summary, we have shown that it is possible to control and manipulate the direction of crack propagation in graphene, and possibly other 2D materials, through engineering the substrate.\(^7^{[18]}\)

4. Experimental Section

Materials: The raw graphite single crystals (NGS Naturgraphit GmbH) were mechanically exfoliated using the “scotch-tape” method and deposited onto a poly(methyl methacrylate) PMMA beams as described in detail elsewhere.\(^3^{[1]}\) It was confirmed that all of the graphene flakes investigated in this study were monolayer from the relative intensities of the 2D and G Raman bands\(^4^{[2]}\) as shown in Figure S4 (Supporting Information).

Microscopy: Optical images were acquired using a Nikon Eclipse LV100ND microscope. Transmission electron microscoe (TEM) images of the edges of exfoliated monolayer graphene flakes were obtained using an aberration-corrected FEI Titan G2 80–200 kV.

Raman Spectroscopy: Raman spectra were obtained using a Horiba LabRAM HR Evolution Raman spectroscopy equipped with a blue Argon ion laser of 488 nm wavelength (\(E_{\text{laser}} = 2.53 \text{ eV}\)). The laser beam was focused on the graphene flakes with a diameter of the laser spot of about 1 \(\mu m\) and the laser power was kept below 1 mW to avoid damaging the graphene. For the in situ deformation tests, the direction of the applied strain was parallel to the incident laser polarization, while the scattered light was not polarized. Deformation was undertaken using a four-point bending rig placed on the stage of the Raman microscope (Figure S1, Supporting Information). The rig was subjected to a fixed displacement so that the PMMA substrate was subjected to constant strain as monitored by a strain gauge, during the Raman measurements. Raman spectra were acquired at different strain levels and mapping was undertaken by obtaining spectra over a square array on the graphene flakes in 1 \(\mu m\) steps for low-resolution maps and 0.5 \(\mu m\) steps for high-resolution maps. The Raman 2D band was fitted using a single Lorentzian function.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

The authors acknowledge support from “Graphene Core 3” GA: 881603 which is implemented under the EU-Horizon 2020 Research & Innovation Actions (RIA) and is supported by EU-financed parts of the Graphene Flagship.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

crack propagation, fracture mechanics, graphene, Raman spectroscopy, stress field

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