

Supporting Information

Strengthening in graphene oxide nanosheets: Bridging the gap between interplanar and intraplanar fracture

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EXPERIMENTAL SECTIONS

MEMS device fabrication, Graphene Oxide (GO) nanosheet preparation, and *in situ* tensile testing

The microelectromechanical system (MEMS) devices were constructed using a standard SOI-DRIE process. The two symmetrical actuation shuttles on the MEMS device have $\sim 2\text{ }\mu\text{m}$ gap which was precision-cut using focused ion beam milling. The GO solution was prepared by the method described in our previous work.¹ Large GO flakes were obtained by slowly stirring the GO solution and a two-step centrifuge process.² After centrifuge, the GO solution (5 mg/mL) was aspirated into a robotic controlled micropipette,³ which can precisely control the volume to dispense of GO solution to the center of two actuation shuttles. After drop-casting, the suspended GO nanosheet was dried in air for one day. The suspended GO nanosheet and MEMS device were baked at 100 °C for one hour to evaporate any residual water molecules. For samples 1, 2, 3, 7, and 8, prior to GO nanosheet thickness measurement by Atomic Force Microscopy (AFM) and tensile testing, the MEMS device was attached and wire-bonded to a printed circuit board. The device was then placed inside the Scanning Electron Microscopy (SEM) (Hitachi SU 3500) to perform tensile tests by applying direct current through the thermal actuator. A voltage step of 0.5 volt was utilized to increment tensile strain. Low voltage electron microscopy (5 keV) and short exposure times to the electron beam were used during SEM imaging and tensile testing to minimize electron beam influence on the GO sample. The vacuum inside the SEM chamber ($< 5\text{e-}3\text{ Pa}$) provided a stable and low humidity environment. Finite element multiphysics simulation of the MEMS device shows that even at a high actuation voltage (5 V), the temperature at the edge of the actuation shuttle only increased by $\sim 55^\circ\text{C}$, suggesting that any thermal effects on the GO samples can be neglected. Tensile tests and imaging of samples 4, 5 and 6 were performed under the same tensile experiment configuration in a Hitachi HF 3300 Environmental-CFE-TEM operated in scanning mode at 100 keV (low beam voltage to minimize electron damage to the sample). MEMS devices used for these samples were back side etched to make them Transmission Electron Microscopy (TEM) compatible. The scanning transmission electron microscope (STEM) images in Figure 2e were taken under the same condition.

Molecular dynamics (MD) simulations

MD simulations were performed using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS)⁴ with interatomic interactions modelled using the ReaxFF potential⁵. The ReaxFF has been implemented in a number of previous experimental-computational studies of the GO system to predict mechanical behavior^{6, 7}. Additionally, MD tensile simulations were performed on defect-free GO nanosheets to validate the ReaxFF potential against previous reports (see Figure S8). GO nanosheets with lateral dimensions measuring at least $8 \times 11\text{ nm}$, and possessing 6 GO layers through the thickness were created for MD simulation. GO layers were stacked in an ABAB configuration, which is consistent with electron diffraction studies of basal plane stacking in bulk GO.⁸ Upon initialization of the atomic topology, the GO nanosheet was heated to 300 K over a 10 ps interval. An additional 10 ps step was also programmed to bring the

sample into an equilibrated configuration. Uniaxial strain-controlled tensile loading was applied by dilating the simulation cell along the armchair direction and simultaneously performing an equal affine transformation to atom positions (LAMMPS; *fix deform* command). This deformation methodology is equivalent to uniaxial loading along the armchair direction. In order to properly capture Poisson effects, the simulation cell was permitted to contract in directions orthogonal to the applied loading. All tensile testing of the GO nanosheet was performed at an equivalent strain rate of $10^9/s$ and stress was defined using the virial theorem. Prior to tensile loading, an elliptical edge crack was introduced in one of the carbon layers by disabling bonding interactions between neighbouring atoms across the crack plane. Bonds were selectively cleaved in order to maintain a zigzag topology on the crack edge, as this atomic configuration is known to possess the highest stability.⁹ Periodic boundary conditions were maintained in the loading and thickness directions. A static fixed boundary with a 1 nm vacuum was enforced along the carboxyl terminated edges of the GO nanosheets. The true cross-sectional width of the GO nanosheet was measured at each loading stage and the virial stress tensor was scaled accordingly to reflect the actual GO volume. A timestep of 0.25 fs was used for all MD simulations and a system temperature of 300 K was maintained using the Nose-Hoover thermostat available in LAMMPS. The Open Visualization Tool (Ovito)¹⁰ was used to visualize atomic topologies.

Other Supporting Information

A) Force Calibration.

Force was calibrated from measuring actuation voltages and displacements of the actuation shuttle, whereby the actuation beams and heat sink beams together act as a spring. The relationship between displacements of the actuation shuttles and applied voltages was first calibrated using SEM imaging. Using Finite Element Modeling (FEM) ANSYS Parametric Design Language (APDL) multiphysics, voltage versus actuation displacement behaviour of the device was simulated using the same boundary conditions as in the real device and with the physical properties defined as silicon. The simulated voltage versus actuation displacement data was then fit using a polynomial curve, which correlates well with data from experimental calibrations, as shown in Figure S1. This indicates that the simulated behaviour of the actuation system can be used to predict the behaviour of the MEMS device. In order to calibrate forces applied to the GO nanosheet, a displacement boundary condition was assigned to the actuation shuttle in the FEM multiphysics model. At a fixed voltage, with different displacement constraints at the actuation tip, the actuation shuttle exhibits a linear relationship between reaction force and actuation displacement, as shown in Figure S2. Displacement data was obtained by measuring digital pixels between the edges of the two actuation shuttles using high-resolution SEM images. In order to show there is no slippage between GO nanosheets and the actuation shuttles during tensile tests, loading/unloading to a strain of 3% was conducted for each sample before loading it to failure. Figure S3 shows the loading/unloading curves of samples 1-5, which all revealed no significant hysteresis. Therefore, there was no significant slippage between the GO nanosheet and the actuation shuttles. The calculated reaction force is then the tensile force applied to the GO nanosheet.

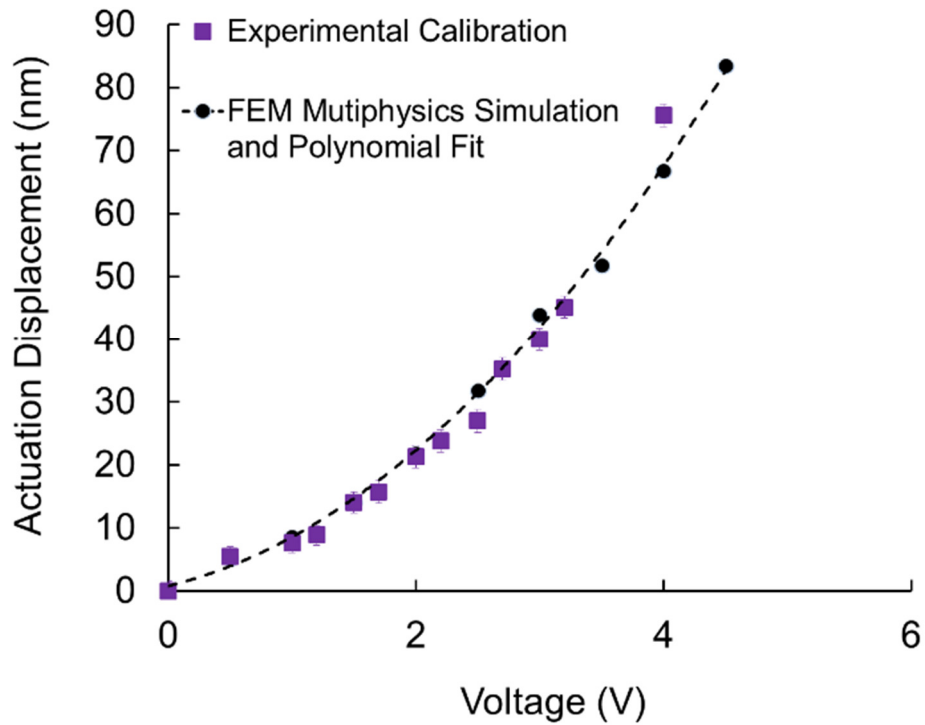


Figure S1: Actuation displacement as a function of applied voltage from experimental calibration in good agreement with that from FEM multiphysics simulation with a polynomial fit.

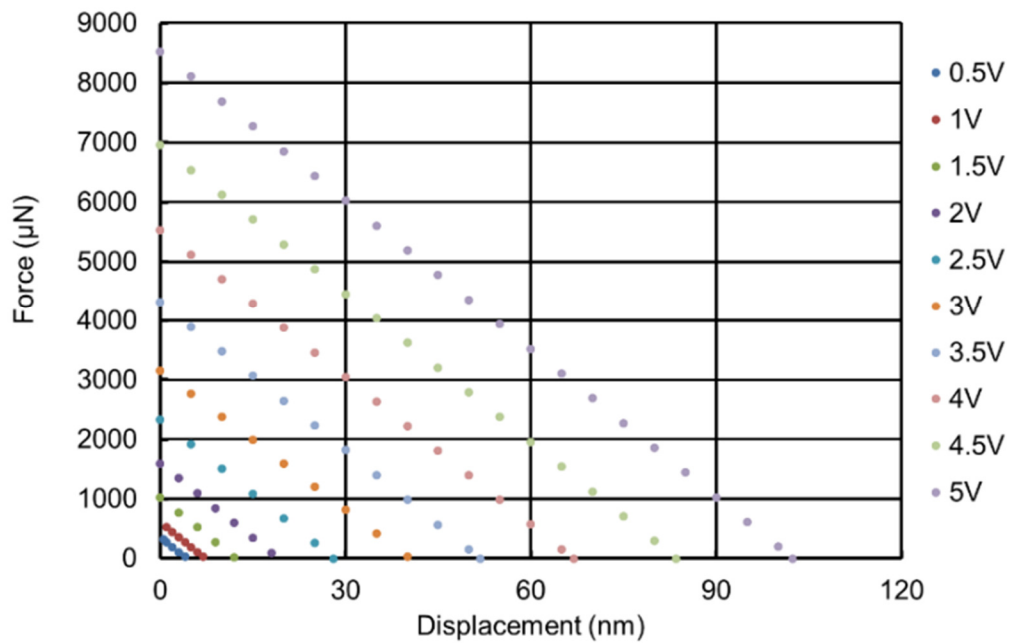


Figure S2: Force displacement response of the MEMS device simulated in FEM APDL multiphysics at different actuation voltages.

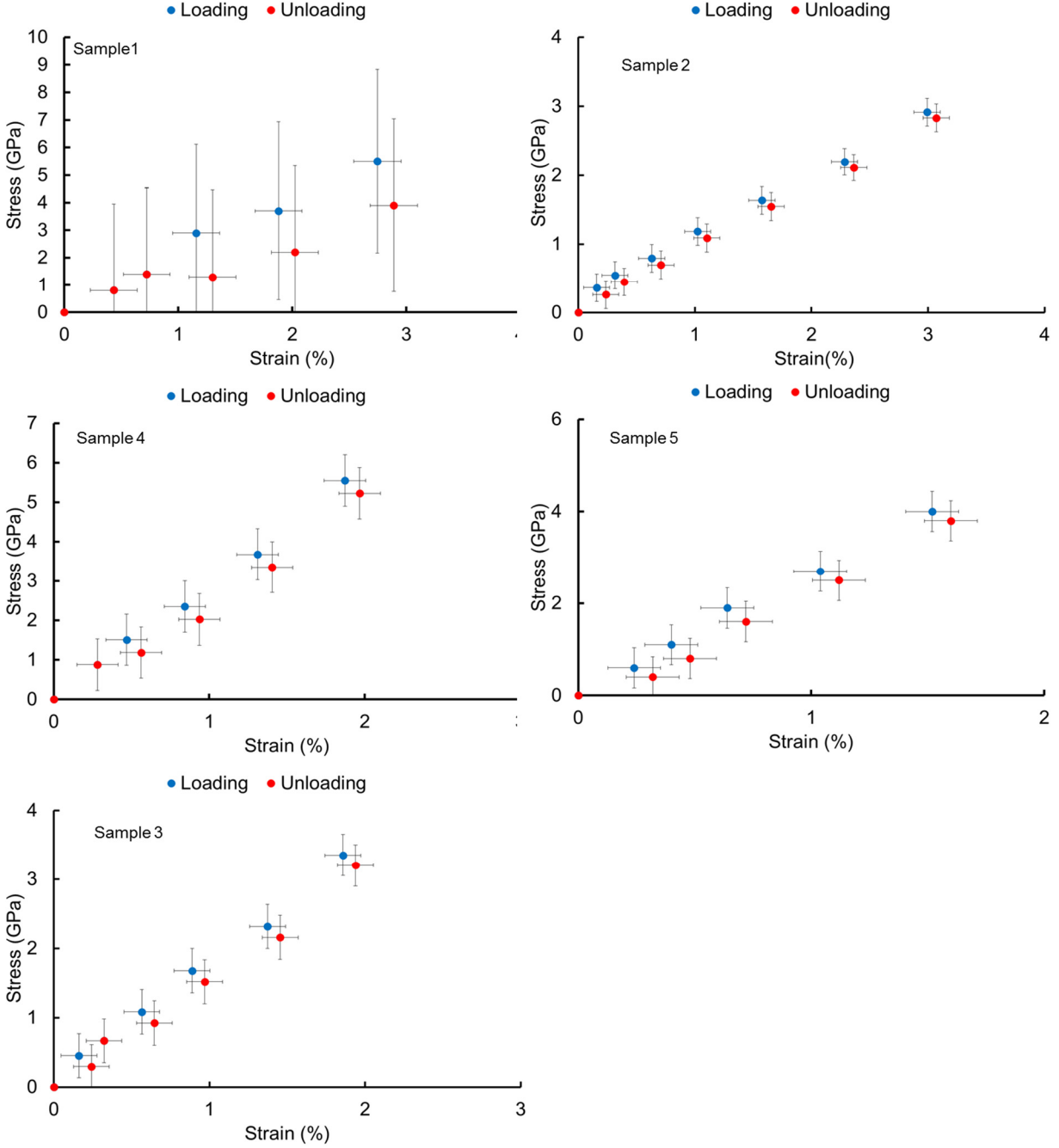


Figure S3: Elastic loading/unloading stress-strain curves of samples 1-5 showing no significant hysteresis.

B) Error Analysis.

Stress (σ) was calculated by dividing the applied tensile force, F , by the cross-sectional area of the nanosheet. The cross-sectional area of the sample was calculated as the product of film thickness (T) and width (W) (Eq. 1). AFM non-contact mode topography scanning was used for the film thickness measurements by measuring the height profile over the edge of the suspended

film on the MEMS device, as shown in Figure 2c. The film width, W , was measured from high resolution SEM images and was assumed to be constant during the entire tensile test. Since the stress estimation involves a combination of independent measurements, propagation of error (standard deviation) was calculated by considering all contributing parameters in Eq. 2. Substituting Eq. 1 into Eq. 2, the final propagation error of the stress was calculated according to Eq. 3.

$$\sigma = \frac{F}{WT} \quad (1)$$

$$\sigma_{\sigma}^2 = \sigma_F^2 \cdot \left(\frac{\partial \sigma}{\partial F}\right)^2 + \sigma_W^2 \cdot \left(\frac{\partial \sigma}{\partial W}\right)^2 + \sigma_T^2 \cdot \left(\frac{\partial \sigma}{\partial T}\right)^2 \quad (2)$$

$$\sigma_{\sigma} = \text{sqrt} \left[\sigma_F^2 \cdot \left(\frac{1}{WT}\right)^2 + \sigma_W^2 \cdot \left(\frac{F}{TW^2}\right)^2 + \sigma_T^2 \cdot \left(\frac{F}{WT^2}\right)^2 \right] \quad (3)$$

where σ_{σ} is stress error; σ_F is force error; σ_W is film width error; and σ_T is film thickness error.

Errors in the contributing parameters were estimated based on the minimum resolution of each measurement technique. Since the error in force determination resulted from the error of shuttle displacement measurement (resolution of 1 pixel = 5 nm in sample 1, and 1 pixel = 2 nm for all other samples), the corresponding force value (Figure S2) was used as the force error at different voltages. The standard deviation of film thickness measurement by AFM was used as thickness error. Film width error was determined by the standard deviation of the width measurement from SEM imaging.

As shown in Eq. 4, strain (ε) is also a combination of independent measurements, including measurements of the initial gap distance (d) and the corresponding stabilized gap distance (d_1) when a voltage is applied. Error in ε can therefore be estimated by Eq. 5. Error for both distance measurements was limited by the digital resolution (*i.e.* one pixel).

$$\varepsilon = \frac{d_1 - d}{d} \quad (4)$$

$$\sigma_{\varepsilon} = \text{sqrt} \left[\left(\frac{\sigma_{d_1}}{d}\right)^2 + \left(\frac{\sigma_d \cdot d_1}{d^2}\right)^2 \right] \quad (5)$$

where σ_{ε} is strain error; σ_{d_1} is stabilized gap distance error; and σ_d is initial gap distance error. Propagated error for effective volume calculations was determined in the same manner as in Eq. 2.

C) AFM imaging of lateral GO Flakes and Cross-sectional imaging of the GO nanosheet.

The lateral dimension of GO flakes was confirmed by drop-casting GO solutions (prepared in the same manner as for tensile testing) on a piece of Si substrate and then imaged using AFM non-contact mode topography scan. The average lateral dimension of the flakes exceeded 1 μm , as shown in Figure S4a.

In order to confirm that the GO nanosheet was well-packed and possessed no voids or defects in the gallery space, a sample was drop-cast on a Si/SiO₂ wafer and cross-sectioned using Ar broad-beam ion milling. Figure S4b presents a high magnification SEM (Hitachi S4800) image of the milled GO nanosheet cross-section. As shown in the figure, the cross-section appears defect free, indicating that the gallery space is indeed well-packed. Additionally, this SEM image supports thickness measurements collected by the atomic force microscopy (AFM) instrumentation.

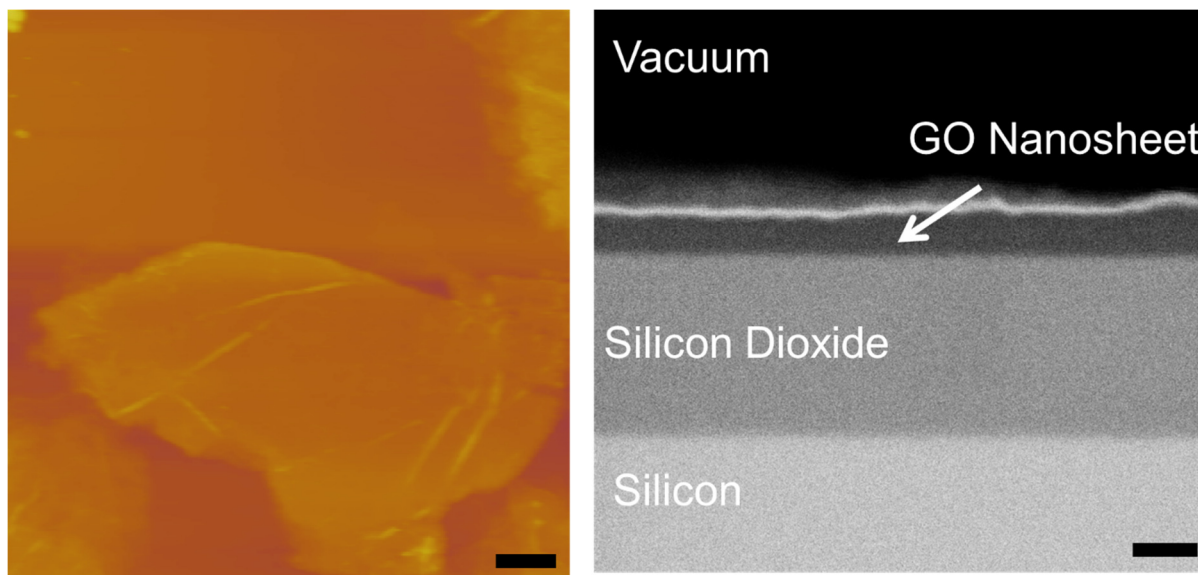


Figure S4: (a) AFM image showing the lateral dimension of GO flakes (scale bar: 1 μm). (b) SEM cross-sectional view of GO nanosheet drop-cast on a Si/SiO₂ wafer. The upper boundary of the nanosheet appears white due to increased electron ejection at the sample edge (scale bar: 100 nm).

D) Electron Energy Loss Spectroscopy (EELS) Thickness Map of GO

In order to validate AFM thickness measurements, electron energy loss spectroscopy (EELS) thickness mapping was conducted on sample 5 using a Hitachi HF-3300 Transmission Electron Microscopy (TEM) operated at 100 keV (low beam voltage to minimize electron damage to the sample). This method allows a direct thickness measurement on the suspended region of the nanosheet by collecting the mean free paths (MFP) electrons passing through the film¹¹. Since

EELS thickness mapping is limited to the TEM field of view (~600 nm by 600 nm), a map montage was collected from the edge to the center of the film. As Figure S5 shows, TEM images were spliced and the fraction of the MFP along the red dashed line was measured. The average number of MFPs of this sample is measured to be 0.32 with a standard deviation of 0.08. Although a quantitative thickness calculation of this film would require the knowledge of mean free path of our GO sample (which is not well known), the ratio of standard deviation to the mean for the EELS and AFM measurements ($0.08\text{mfp}/0.32\text{mfp}$ versus $14\text{nm}/34\text{nm}$) indicate that the AFM measurements and the associated error provide an upper bound estimate on the error in the GO nanosheet thickness. Consequently, the error propagated into the stresses and strengths derived from these values represent a conservative estimate of the measurement error.

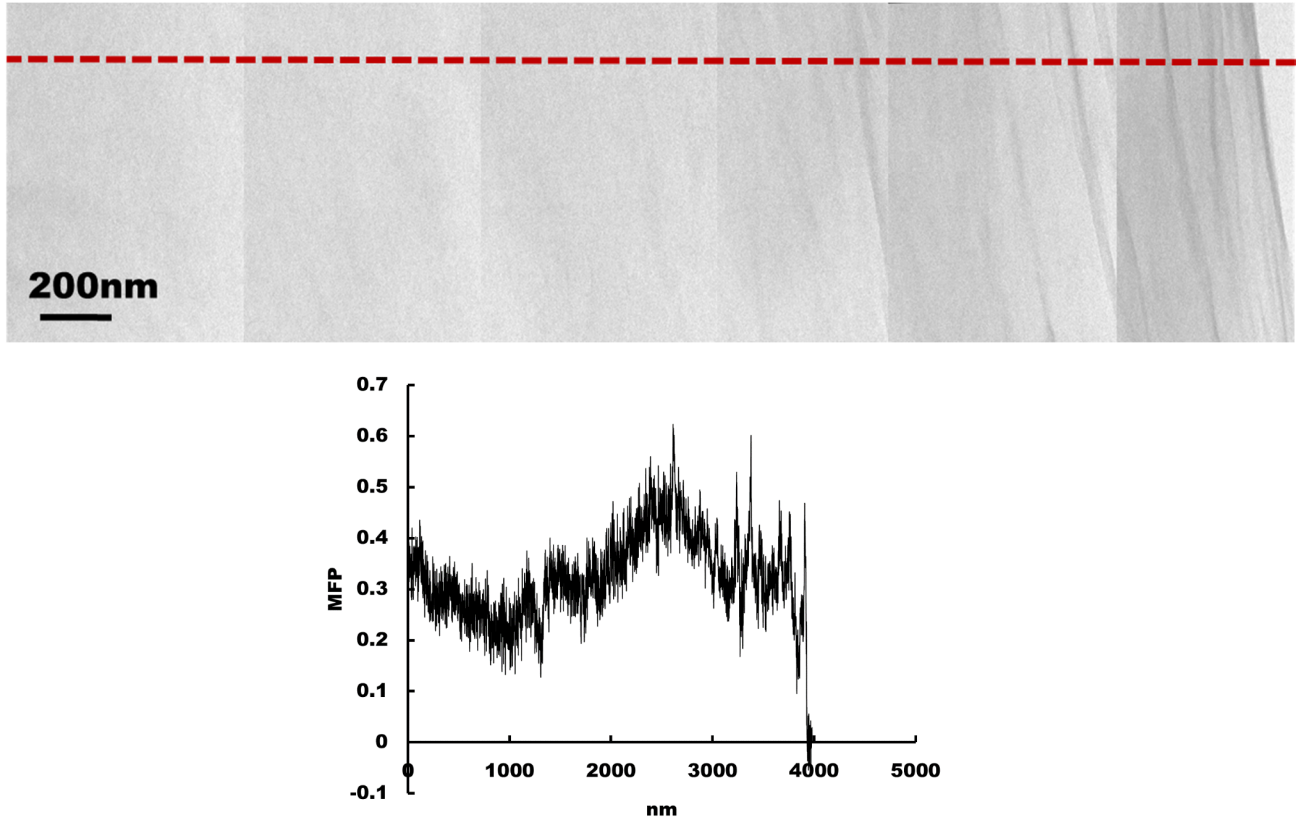


Figure S5: (Top) Spliced TEM images of GO film. (Bottom) MFP profile along the red dash line indicated in the top image.

E) GO samples with large pre-existing crack

Figure S6 shows a representative sample which has a large pre-existing crack before tensile test (sample 7). Due to this critical crack in the sample, the strength and modulus of this sample cannot be measured. However, the subsequent fracture mechanism for samples with large pre-existing cracks was found to be consistent with the pristine cases.

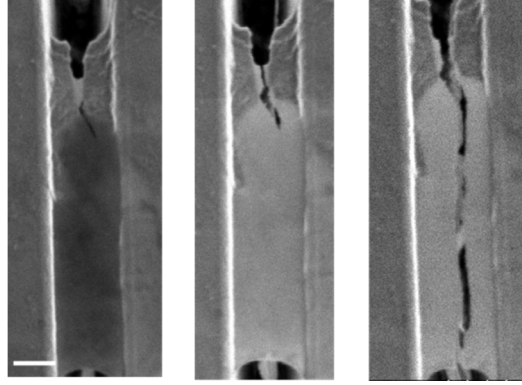


Figure S6: GO sample with large pre-existing cracks (Sample 7). (Scale Bar: 1 μm)

F) Additional Experimental Data.

Figure S7 shows SEM images of the evolution of failure initiation and crack propagation in sample 3. Failure initiated at the edge of the nanosheet at a strain of $\sim 3\%$ and with an ultimate tensile strength of 6 ± 1 GPa. Once failure initiated, a crack propagated through the entire width of the nanosheet. The angle between fracture path and the tensile loading direction was measured for each sample from SEM images and defined as the angle rotating counter-clock wise from the tensile loading direction to the direction of the fracture path. The error in the angle measurement resulted from variations of the fracture path (see Figure S7).

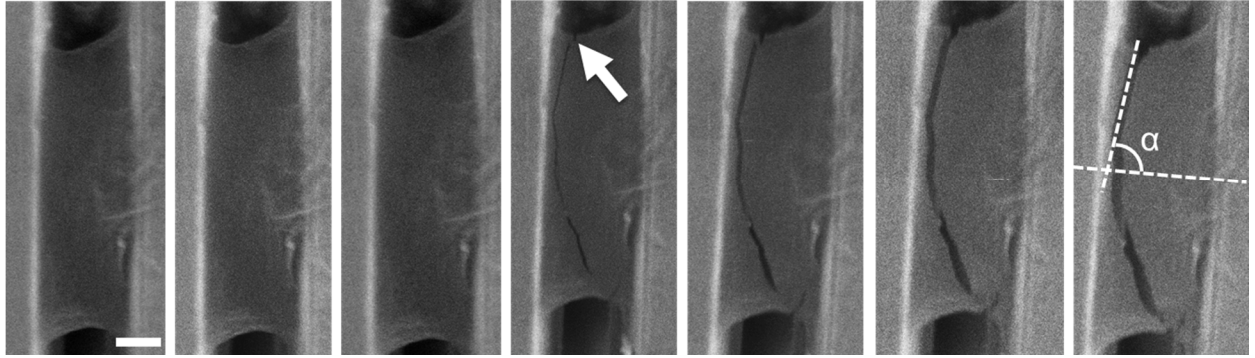


Figure S7: SEM images documenting GO nanosheet failure under uniaxial loading of sample 3. Arrow pointing the initiation of failure on the edge of the GO nanosheet. α is measured to be $90^\circ \pm 10^\circ$, is the angle rotating counter-clock wise from the tensile loading direction to the linear fitted fracture path. (Scale bar: 1 μm)

G) Collected structural and mechanical properties of the GO nanosheets.

The geometrical measurements required to calculate stress-strain curves as well as the relevant mechanical properties and fracture path angles for all samples in this study are summarized in Table S1.

Table S1 Geometric measurements and tensile test results of GO nanosheet samples.

Sample #	Sheet Thickness (nm)	Cross-Sectional Width (nm)	Suspended Sheet Length (nm)	Young's Modulus (GPa)	Tensile Strength (GPa)	Fracture Path Angle (degree)
1	75 ± 13	909 ± 33	1730 ± 5	204 ± 7	12 ± 4	89 ± 3
2	70 ± 11	9152 ± 90	1966 ± 2	103 ± 5	4 ± 1	87 ± 5
3	65 ± 9	7160 ± 45	2204 ± 2	182 ± 3	6 ± 1	90 ± 10
4	24 ± 4	7990 ± 242	1616 ± 2	291 ± 5	11 ± 1	87 ± 2
5	34 ± 14	8494 ± 14	1893 ± 2	266 ± 5	8 ± 1	85 ± 5
6 ^a	68 ± 9	2550 ± 63	3920 ± 2	--	--	89 ± 4
7 ^b	48 ± 7	7569 ± 50	1773 ± 2	--	--	87 ± 4
8 ^b	51 ± 10	7306 ± 44	1312 ± 2	--	--	88 ± 3

^aSample was used for imaging purposes, no stress-strain data was collected

^bYoung's modulus and tensile strength cannot be accurately reported due to large pre-existing cracks.

H) Tensile Simulation of Defect-Free GO Nanosheets.

In order to validate the ReaxFF potential, MD simulations of defect-free GO nanosheets (*i.e.*, GO nanosheets without any pre-cracked layers) were undertaken. Figure S8 presents the results of uniaxial testing on defect-free 22% hydroxyl functionalized GO nanosheets. From the presented data, a strength of approximately 47 GPa was calculated. Additionally, the elastic modulus (E) is determined by fitting the linear region of the stress-strain curve and was calculated to be approximately 454 GPa. Conceptually, strength measurements of defect-free GO nanosheets should be comparable to monolayer GO strengths, as both materials fail by a similar intraplanar fracture mechanism. Density functional theory (DFT) calculations performed in our previous study for ~20% hydroxyl functionalized monolayer GO predict an intrinsic strength of 36 GPa and an elastic modulus of 386 GPa under armchair loading ¹. Discrepancies between the values determined for GO nanosheets and monolayer values are likely due to assumptions of flake thickness when converting 2D planar values to 3D stresses. For example, 0.7 nm is often chosen as the thickness of monolayer GO ¹², whereas the layer thickness in the present simulations is approximately 0.55 nm (*i.e.* number of layers divided by cross-section thickness of the MD supercell) which increases effective stress values by ~ 27%. GO is known to possess interplanar spacings in the range of 0.6 – 1.2 nm ¹³, making the definition of a specific monolayer thickness problematic. If a 0.7 nm layer thickness were assumed in the current MD simulations, the

resulting armchair strength and elastic modulus is 37 GPa and 356 GPa, respectively. These adjusted estimates are in excellent agreement with previous DFT results. It should also be noted that MD predictions of mechanical properties are much higher than experimental values due to the pristine nature of the simulation topology as well as the artificially high strain rates which are utilized in MD simulations. Planar defects in the GO nanosheets tested experimentally led to significantly reduced stiffening during loading and reduced overall tensile strength.

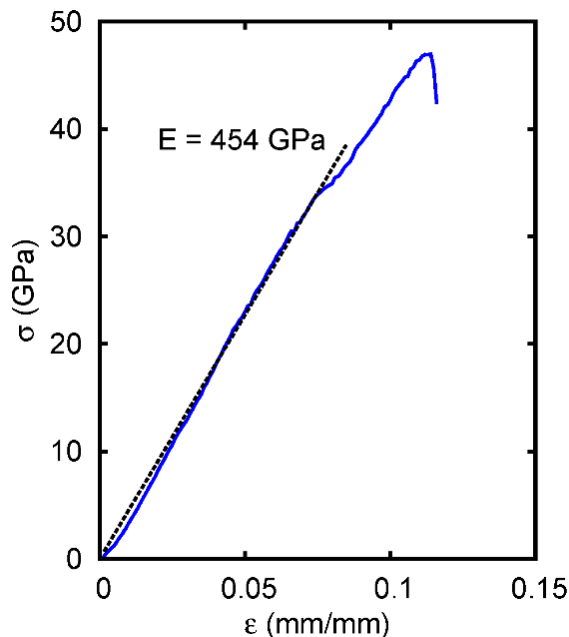


Figure S8: Stress-strain response of a defect-free GO nanosheet subjected to uniaxial tensile loading. The dashed line represents a best-fit to the linear region of the stress-strain curve, providing an estimate for the elastic modulus of 454 GPa.

I) Undulations and strain-induced corrugations in GO Nanosheets.

Relaxation of hydroxyl functionalized GO nanosheets led to the agglomeration of functional groups. The kinetics of this phenomenon is consistent with previous first principles calculations¹⁴ and TEM observations¹⁵. These functional group agglomerates were randomly distributed across the sample and measured approximately 1-2 nm in size. The collection of functional groups created undulations in the carbon basal planes (Figures S9a and c). The peaks and valleys of these undulations were found to range between 0.4-0.7 nm in amplitude. As shown in Figures S9b and d, localized undulations were observed to align into long-range corrugations perpendicular to the applied strain. Figures S9e and f show histograms of the functional group distribution across the zigzag dimension (L_x) of the layer. Clearly, the formation of pronounced corrugations encourages the collection of agglomerates within the basins, creating areas of excess and dearth of functional groups. These functional agglomerates are then confined within strain corrugations upon sustained loading. The geometric effect of this confinement can create

a strain localization within layers adjacent to an edge crack from strain energy release during flaw propagation.

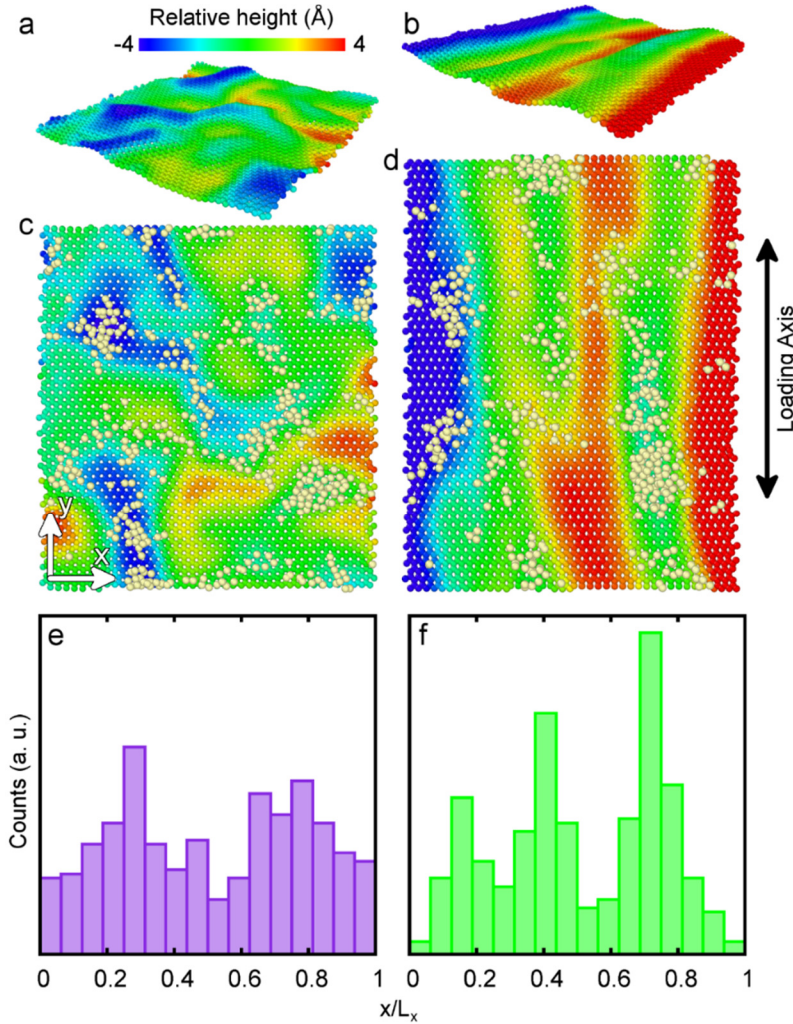


Figure S9: The surface profile of a single layer in the hydroxyl functionalized GO nanosheet in perspective (a), (b) and planar (c), (d) views prior to uniaxial deformation in MD simulations (a), (c), and just before fracture of the GO nanosheet (b), (d). The selected layer is adjacent to a pre-cracked layer. For clarity purposes, functional groups are removed from (a) and (b), and only oxygen is displayed in (c) and (d). The original distribution of functional groups (e) is observed to rearrange, with functional group agglomerates collecting in basins created by the strain-induced corrugations (f).

J) Fracture of GO Nanosheets with an Edge Crack.

In order to understand failure mechanism in GO nanosheets, we assumed an elliptical edge crack to be present in the MD topology due to presence of a critical manufacturing flaw. A schematic of the construction methodology and parameter definition of the cracks is presented in Figure S10a. Figures S10b-d show fracture propagation in GO nanosheets with edge cracks in a single layer measuring $2a_o$, $4a_o$, and $8a_o$, where a_o is the width of the hexagonal unit cell along the zigzag direction in the carbon basal plane. In all MD simulations, a consistent Mode I fracture

mechanism was observed whereby the elliptical edge crack propagated perpendicular to the applied loading. Fracture was preceded by the development of a highly confined stress concentration around the leading edge of the crack, which is consistent with the absence crack-tip plasticity and a brittle fracture mechanism (Figure S11). The stress intensity factor may be determined by considering the ratio of the maximum stress at the crack-tip to the applied far-field loading. Under this definition, stress intensity factors of 2.3, 3.8 and 4.9 were calculated for GO nanosheets with pre-defined edge cracks measuring $2a_o$, $4a_o$, and $8a_o$, respectively.

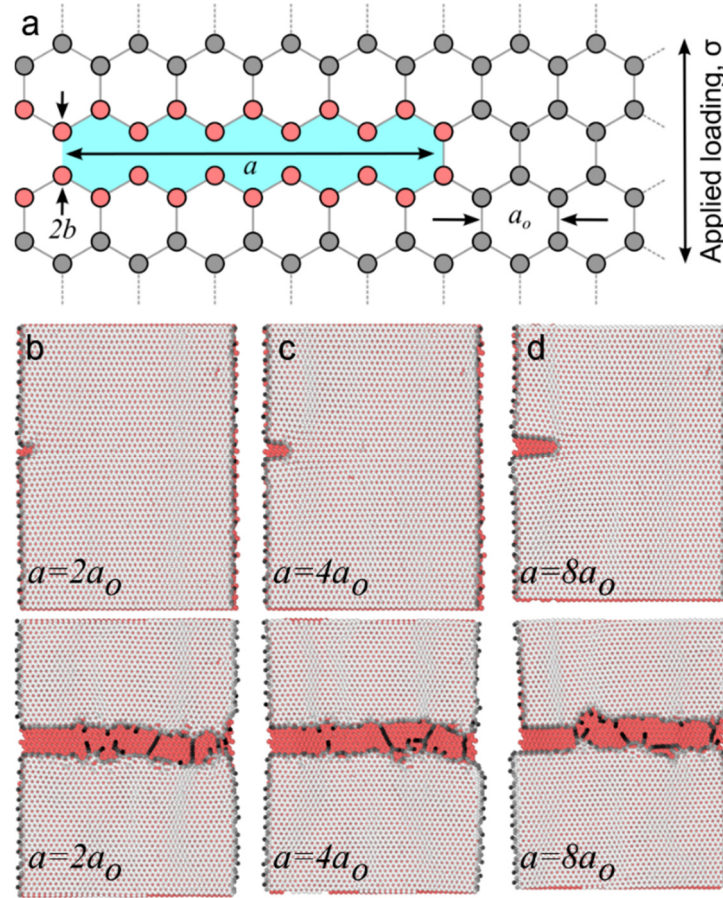


Figure S10: (a) The structural parameters used to define and classify edge cracks in MD simulations conducted in this study. (b)-(d) Snapshots of elliptical edge cracks in the GO nanosheet pre- and post-failure. Atoms in the pre-cracked layer are colored based on their local coordination, with darker shades corresponding to an under-bonded condition. The adjacent carbon basal plane is visible in each of these images (pink). For clarity, the functional groups are hidden in these images.

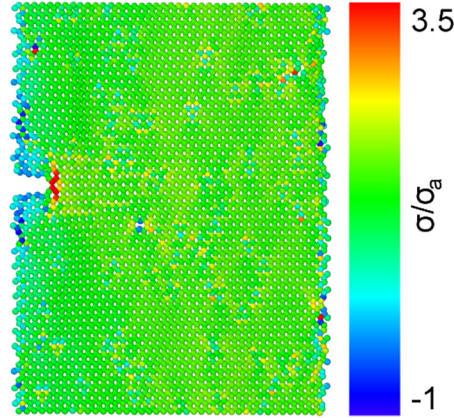


Figure S11: The atomic stress map in the pre-cracked layer ($a = 4a_o$) of a GO nanosheet just prior to fracture. The color map shows the ratio of atomic stress to the average applied stress in the layer (σ_a). For clarity purposes, the functional groups are hidden in this image.

K) Elastic Energy Release Rate in GO nanosheets.

As a brittle material, the elastic energy release rate of GO nanosheets may be determined within the context of Griffith crack theory¹⁶ under a plane stress assumption. Under this framework, the elastic energy release rate (G_{IC}) in response to Mode I failure of an elliptical crack may be calculated as¹⁷:

$$G_{IC} = \frac{\sigma_f^2 \pi a}{E} \quad (6)$$

where σ_f is the fracture stress of the sample, a is the half-length of the crack and E is the elastic modulus. As mentioned above, MD simulations showed a consistent Mode I fracture behaviour. In order to determine G_{IC} , a sequence of MD tensile simulations with varying edge crack lengths were performed. This series of MD simulations was performed on 22% hydroxyl functionalized monolayer GO, using the methodology described in the experimental section. Figure S12 plots the G_{IC} values against crack length. G_{IC} was found to increase monotonically with crack length until reaching a plateau at larger values of a . It should be noted that within the context of Griffith theory, G_{IC} should be a constant. However, at low values of a , the edge crack possesses a low eccentricity and blunt profile, making the application of Griffith theory somewhat inaccurate. This behaviour has been noted in other MD studies of atomic-scale crack propagation¹⁸. With respect to crack profile, the ratio of the major and minor axes of the crack ($2a/b$), may be considered as a measure of eccentricity. As shown in the figure, G_{IC} appears to stabilize with $2a/b > 5$, which appears to be the threshold for application of the Griffith criterion. Averaging of G_{IC} values above this limit results in a G_{IC} of 13.1 J/m², which approaches the experimental value for graphene (15.9 J/m²)¹⁹. An elastic modulus of 454 GPa was assumed for all energy release rate calculations.

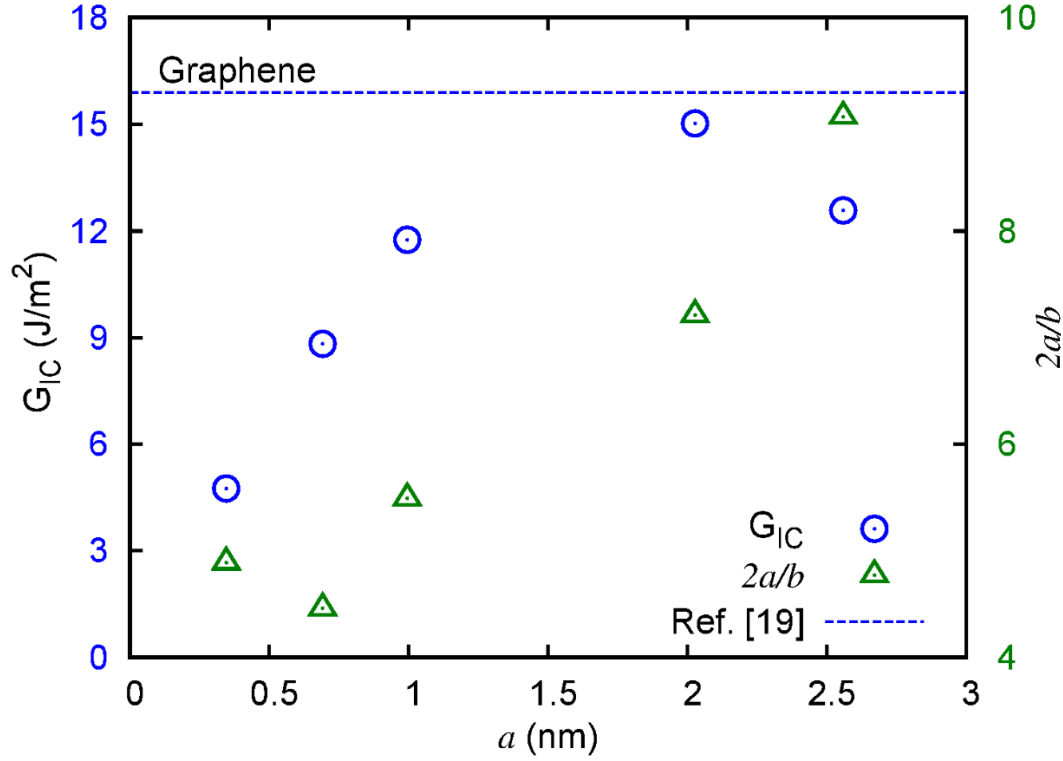


Figure S12: Elastic energy release rate of monolayer GO for varying edge crack lengths. The eccentricity of the crack profile is plotted on the secondary axis. The experimental G_{IC} for graphene (15.9 J/m²) is provided as an upper threshold for comparison to the current MD calculations.

L) Fracture in Epoxide Functionalized GO Nanosheets.

Although the nanosheets are expected to be hydroxyl functionalized due to the metastability of epoxide groups in GO²⁰, MD simulations were performed to observe any transitions in fracture behaviour resulting from epoxide functionalization. As with the hydroxyl GO nanosheets, a 22% functionalization was assumed. MD simulations were performed as described in the experimental section. Figure S13 presents the failure progression in a GO nanosheet with a pre-cracked layer ($a = 4a_o$). Perspective and cross-section images of the relaxed GO nanosheet are provided in Figures S13a and 13b respectively. Figure S13c illustrates fracture propagation across the pre-cracked layer. The atomic strain map of the layer adjacent is also visible. In contrast to hydroxyl functionalized GO, propagation of the edge crack does not result in a strain concentration near the fracture path in the adjacent layer. As shown in the figure, fracture in the adjacent layer is uncorrelated to a specific strain concentration and is observed to occur along a path comprised of pre-existing point defects (Figure S13d).

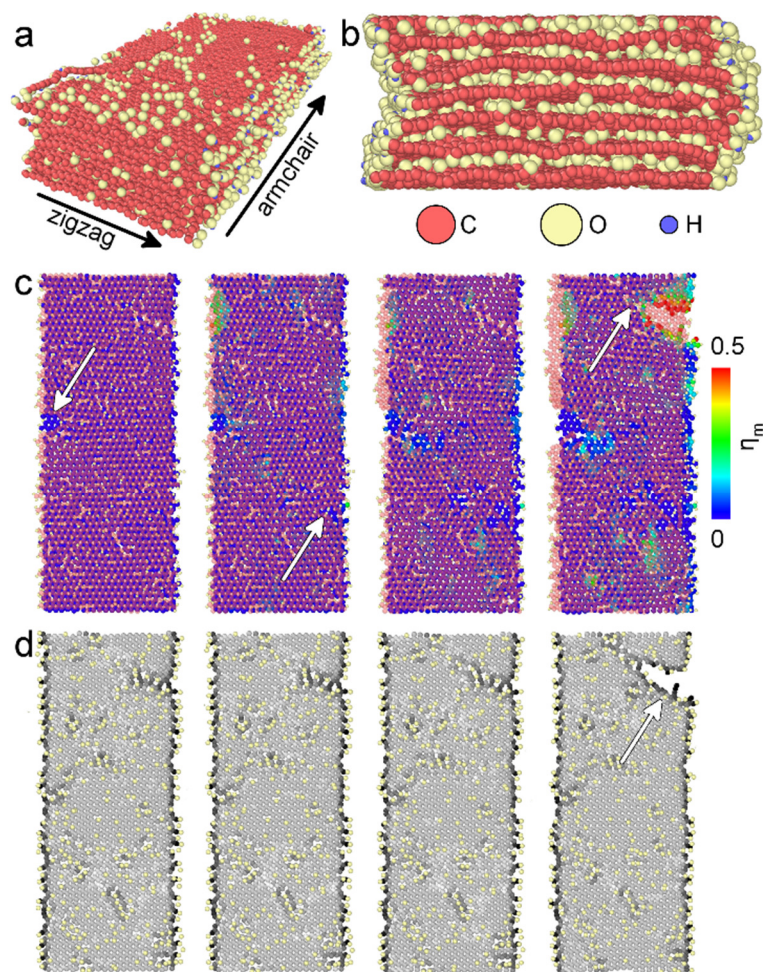


Figure S13: Perspective (a) and cross-section (b) views of the epoxide functionalized GO nanosheet. (c) Fracture propagation in the pre-cracked layer ($a = 4a_o$) which appears pink and translucent. Fracture events in epoxide GO appear to follow a path formed by critical planar flaws which are introduced by the functional groups during loading. The atomic strain map in the adjacent layer is also visible. Atomic strain is defined here as describe in the main text. (d) Coordination map of the adjacent layer at the same loading states as (c). The color map in (d) is applied in the same manner as describe in Figure S10. Fracture is uncorrelated to the above crack and initiates from a path comprised of critical planar flaws. Arrows indicate independent fracture events.

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