Supporting data for
On the structure and topography of free-standing chemically modified graphene

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S1. Height-height correlation function

Consider a surface the height of which is defined by the function \( h(x) \), where \( x \) is a two dimensional vector. The height-height correlation function (HHCF) is defined by

\[
H(r) = \left\langle \left( h(x + r) - h(x) \right)^2 \right\rangle
\]

(S1)

where \( r \) is also a two dimensional vector. If the root mean square roughness of the surface is \( \sigma \), and the correlation length \( l_c \), then

\[
H(r) \rightarrow \begin{cases} 
0 & \text{for } r \rightarrow 0 \\
2\sigma^2 & \text{for } r \gg l_c 
\end{cases}
\]

(S2)

The HHCF is closely related to the autocorrelation function.

In atomic force microscopy the tip raster scans across a sample with a fast scan direction in which its scan rate is around 1 line per second and around 2 ms per pixel, and a slow scan axis with a frame rate of around 1 frame per 10 minutes. Changes to the tip apex result in height differences between consecutive lines which cannot easily be accurately removed. As a result it is more robust to use a discrete one-dimensional HHCF in the direction of the fast scan axis, which is averaged over all the lines in the slow scan axis direction. The 1D discrete HHCF used in this work was defined by

\[
H(x_m) = \frac{1}{N(N-m)} \sum_{l=1}^{N-m} \sum_{n=1}^{N-m} \left( h_{l+n,m,i} - h_{n,i} \right)^2
\]

(S3)

where \( n \) is the pixels in the fast scan direction, \( l \) are the lines in the slow scan direction, \( N \) the number of pixels in each line and \( x_m = \delta m \) (\( \delta \) is the pixel separation in the fast scan direction). For more information see [S1, S2]. Figure S1 shows the images/HHCF for (a)/(c) GO on silicon oxide, (b)/(d) GO on mica, (e)/(g) silicon oxide and (f)/(h) mica. The similarities between the bare silicon oxide substrate and the GO on silicon oxide are clear. GO on mica is significantly and consistently rougher than the bare mica.
Figure S1. 500 nm square AFM height images of (a) graphene oxide on silicon oxide, (b) graphene oxide on mica, (c) silicon oxide and (d) mica. The full height-scale for all the images is 3 nm. (c), (d), (g) and (h) are plots of the height-height correlation function for the respective height images. Data extracted from the images is given by the black markers, the solid red lines are fits to the data as described in the main text.
S2. **AFM of suspended single layer graphene oxide**

As described in the main text, suspended single layer graphene oxide sheets were studied by AFM. Due to the flexibility of the single layer GO sheets, the AFM tip could be expected to deform the GO creating artefacts in the height images. Repeated images of the same place gave similar features suggesting this is unlikely, but the most compelling evidence that the observed topography is not an artefact of the imaging process comes from images acquired simultaneously. In constructing an AFM image the AFM tip raster scans across the sample, images are constructed from the tip moving in the same direction i.e. as the tip either moves forwards (trace) or back again (retrace). Figure S2 shows the height images collected simultaneously; (a) is the trace and (b) the retrace image. The similarity between the images is clear. This indicates that the features are not due to the direction the tip scans across the sample or to random noise (which would lead to uncorrelated trace and retrace images), and that the features are static. Figure S2 (c) and (d) are the phase and amplitude images taken simultaneously in the trace direction, the information in them is complementary to the height data and consistent with the interpretation above.

![AFM images](image_url)

**Figure S2.** 750 nm square AFM height images of graphene oxide on silicon oxide; (a) tip moving in the trace direction and (b) the same image with data collected in the retrace direction. The full height-scale for both images is 1.5 nm. The (c) phase and (d) amplitude signals were collected simultaneously in the trace direction.
S3. Tilt series analysis of single and double sheet graphene oxide

Figure S3 plots the fractional peak width of the \((hk) = (11)\) diffraction peak as a function of tilt angle for double layer (black) and single layer graphene oxide (red). Both results were taken on the same GO TEM grid at an accelerating voltage of 140 kV. The solid blue line is a simulation as described in the main text; \(A_r = 0.1, l_{ec} = 5.0 \text{ nm} \) and \(\lambda_c = 20d\). Both show a nonlinear dependence of peak width on tilt angle. At low tilt angle the single layer is broader than the double layer. This is due to a difference in the electron beam coherence length between the two measurements: experimentally this corresponds to a difference in the divergence of the electron beam. At larger tilt angles the widths are similar indicating that the short range topography of the individual sheets is the same independent of whether they are isolated or stuck together. This is in marked contrast to graphene where the broadening of bilayer graphene was found to be significantly less than the broadening of monolayer graphene \([S3, S4]\).

Figure S3. Plot of the change with tilt angle of the fractional peak widths of the Gaussian fits to the \((hk) = (11)\) diffraction peaks of double sheet (black) and single sheet (red) graphene oxide. The solid blue line is a simulation as described in the main text; \(A_r = 0.1, l_{ec} = 5.0 \text{ nm} \) and \(\lambda_c = 20d\).
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S4. **Tilt series analysis of reduced graphene oxide at room temperature and 133 K**

Figure S4 plots the fractional peak width of the \((hk) = (11)\) diffraction peak as a function of tilt angle for single sheet reduced graphene oxide at 133 K (black) and room temperature (red). Both results were taken on the same single layer sheet of graphene oxide at an accelerating voltage of 200 kV. Both show a nonlinear dependence of peak width on tilt angle consistent with the results for graphene oxide and in contrast to the results reported for graphene [S3, S4]. It appears that the sheet is tilted relative to the TEM grid, and hence the minimum peak width is at a tilt angle of around 0.1 radians. The subsequent broadening at higher tilt angles is less rapid than that reported above in figure S3, and less than the data reported in the main article, but not significantly so. This could indicate a slight decrease in roughness after chemical reduction. Further experiments are being undertaken to determine the extent of the change in structure induced by both chemical and thermal reduction.
S5. Analytical approach to diffraction from a 1D lattice with sinusoidal distortion.

Far-field diffraction from a 1D lattice is defined by

\[ \Phi = f(\theta) \sum_n \exp\left[-i(k - k') r_n\right] \]

\[ I = \Phi^* \Phi \]  
(S4)

where \( k \) and \( k' \) are the incident and scattered electron beam wavevectors, \( r_n \) are the atom positions, and \( f(\theta) \) is the scattering factor. The sum is over all atom positions. Considering a sinusoidal ripple on the 1D lattice, with amplitude \( A \) and wavevector \( k_{\text{rip}} \), at tilt angle \( \alpha \) this becomes

\[ \Phi = f(\theta) \sum_n \exp\left[-i nk_c \left(\sin(\alpha + \theta) - \sin \alpha\right)\right] \exp\left[-ik_c A \left(\cos \alpha - \cos(\alpha + \theta)\right)\right] \]  
(S5)

where \( k_c \) is the magnitude of the electron beam wavevector. This can be written in the more familiar form

\[ \phi = \frac{2}{k_{\text{rip}} d} \int_0^d dy \cos\left[ay + b \sin y\right] \]

\[ a = \frac{k_c}{k_{\text{rip}}} \left(\sin(\alpha + \theta) - \sin \alpha\right) \]

\[ b = k_c \left(\cos \alpha - \cos(\alpha + \theta)\right) \]

\[ c = k_{\text{rip}} d \]  
(S6)

for small \( \theta \) and large \( N \) this can be approximated by

\[ \phi \approx \frac{2cN}{k_{\text{rip}} d} J_0(B) \]  
(S7)

where \( J_0 \) is the zeroth order Bessel function. This function has 'satellite' peaks with spacing

\[ \frac{d}{\lambda_{\text{rip}}} \]  
(S8)

and amplitude proportional to \( A \sin \alpha \).
S6. 1D numerical simulations

We consider distortions out of the plane of the graphene sheet. For simplicity and to minimise computational expense a 1D lattice is used where the 'atoms' on the 1D lattice represent the lattice planes in 2D with period \( d \) corresponding to \( d_{\text{hk}} \). Equation (2) from the main text describes scattering from the distorted lattice, incorporating the effect of tilt (\( \alpha \)), and expanding to first order in the scattering angle, \( \theta \):

\[
\Phi = f(\theta) \sum_n \exp\left[-i(n \cos \alpha - A_n \sin \alpha) k \theta \right]
\]

(S9)

where \( A_n \) is the out-of-plane displacement of the \( n \)th atom and \( k \) is the magnitude of the electron beam wavevector. \( f(\theta) \) is the scattering factor for carbon taken from Doyle and Turner [S5]. The ripple function is defined as

\[
A_n = A_r \frac{2N_{\text{atom}}}{2N_{\text{atom}}} \sum_{m=1}^{2N_{\text{atom}}} B_m \sin \left[ \frac{2\pi nd}{\lambda_c + md} + \phi_m \right]
\]

(S10)

where \( B_m \) and \( \phi_m \) are random numbers, and \( A_r \) defines an average roughness. \( \lambda_c \) sets the minimum wavelength of the ripple. Once the rippled lattice is generated the scattering intensity is calculated via

\[
\Phi(\theta, \alpha) = \exp \left( \frac{-nd \cos \alpha}{\lambda_c} \right)^4 f(\theta) \sum_{n=N_{\text{max}}}^{N_{\text{max}}} \exp\left[-i(n \cos \alpha - A_n \sin \alpha) k \theta \right]
\]

\[
I = \left| \Phi \right|^2
\]

(S11)

where the prefactor includes the effect of the electron beam coherence length. The intensity is calculated over a range of tilt angles and scattering angles. To simulate the effect of the size of the aperture the intensity was averaged over at least 100 rippled lattices for each parameter set. The average intensity was then fitted using a Gaussian peak shape for each tilt angle, and the width and height of the Gaussian extracted.

Figure S5 shows contour plots of the diffraction intensity as a function of tilt angle and relative scattering angle

\[
\theta^{\text{rel}}(\alpha) = \theta - \frac{\lambda_c}{d \cos \alpha}
\]

(S11)

The effect of a single sinusoidal ripple is show in figure S5 (a); in accord with section S5 satellite peaks appear and grow in strength as the tilt angle increases. The diffracted intensity due to one randomly generated ripple structure is shown in figure S5 (b), satellite peaks are visible and at tilt angles greater than 0.25 radians it is no longer a simple diffraction peak. The effect of averaging over > 100 rippled lattice samples is evident in figure S5 (c); a single peak is now observed which becomes significantly broader with increasing tilt angle.
Figure S5. Contour plots of the diffraction intensity as a function of the scattering angle and tilt angle. The relative scattering angle is such that 0 radians corresponds to the expected scattering angle. (a) Diffraction intensity due to a 1D lattice of period $d_{11}$ with single sinusoidal ripple of amplitude $0.5 \ a_{cc}$, a wavelength of $\lambda = 11 \ d_{11}$. Diffraction intensity due to a random Fourier series distortion $A_r = 0.1$, $l_c = 5.0 \ nm$ and $\lambda_c = 20 \ d$ with (b) one sample and (c) averaging of more than 700 samples.
S7. References
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S5. Doyle P A and Turner P S 1968 Relativistic Hartree-Fock X-ray and electron scattering factors Acta Crystallographica Section A 24 390-7