Very large scale characterization of graphene mechanical devices using a colorimetry technique

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Electronic Supplementary Information

Electronic Supplementary Information Outline:

1. Fabrication of SLG and DLG drumheads.

2. Colorimetry Technique.

3. Derivation of the expression for adhesion energy.

4. Raman spectroscopy of suspended and collapsed DLG drumheads.

5. Theoretical limit of large-diameter drums before collapse.

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1. Fabrication of SLG and DLG drumheads.

Single-layer graphene was grown by chemical vapour deposition (CVD) using a 4” cold wall reactor (Aixtron BM). Copper foil was used as the catalyst and a surface pre-treatment was carried out in order to remove the native copper oxide and other impurities. The synthesis was carried out at $1000°$C using methane as the carbon source. After the synthesis, the single-layer graphene (SLG) was coated with a polymer layer and stacked onto a second single-layer graphene by using a semi-dry transfer process. The stacked CVD double-layer graphene (DLG) was transferred onto $5{\times}5$ mm^2 SiO_2/Si substrates containing circular cavities by following a semi-dry transfer procedure. Finally, the supporting polymer layer was removed by annealing at $450°$C for 2 hours in N_2 atmosphere.

2. Colorimetry technique.

An OLYMPUS BX60 optical microscope with Khler illumination is used with its halogen lamp as the effective multiwavelength white light source. Pictures are taken using an infinity corrected $20\times$ objective lens (OLYMPUS UMPlanFI) with a numerical aperture of 0.46 and a 3 mm working distance. A consumer camera (Canon EOS 600D) collects images of the sample in a monochrome RAW format. These images are later corrected for the Gamma compression that is inherent to CMOS imagers [S-1, S-2] as:

$$I = 255\left(\frac{I_{RAW}}{255}\right)^{2.2}. \tag{1}$$

A series of color filters (Thorlabs FL460, FLH532, FB600, FLH633, FBH660) are mounted on a motorized computer-controlled wheel, and placed in front of the camera imager as shown schematically in Fig. S1. Under the $20\times$ magnification it is possible to observe 500-1000 graphene drums simultaneously (depending on their diameter), as shown in the example image in Fig. S2. Thus for each of the samples, that contains 3016 cavities, a total of three optical microscope images per color filter are enough.

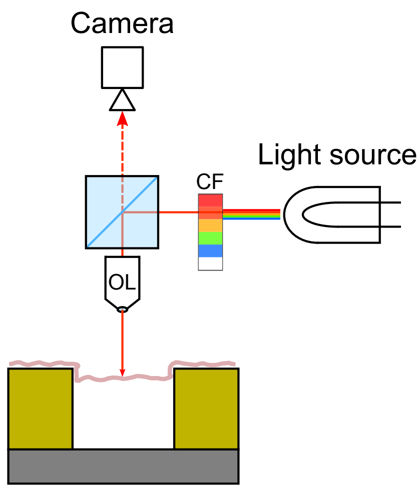

Figure S-1: Colorimetry setup: an optical microscope with Köhler illumination and a 20× objective lens (OL) is used for visualizing the suspended graphene drums. The white light illumination of a halogen lamp goes through a color filter (CF).

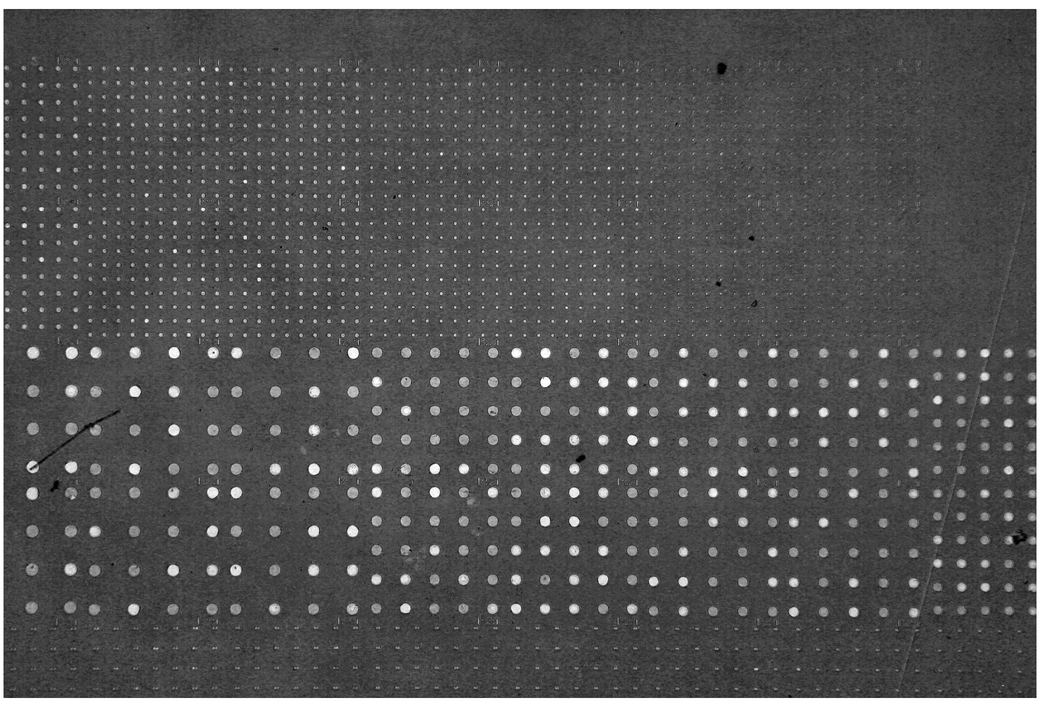

Figure S-2: Example of an optical microscope picture taken with 460 nm color filter. Nearly 1000 drums of varying diameters are seen.

3. Derivation of the expression for adhesion energy.

We approximate the stuck region of the drum to a circular region concentric with the circular drum, and assume perfect clamping as shown in Fig. S3.

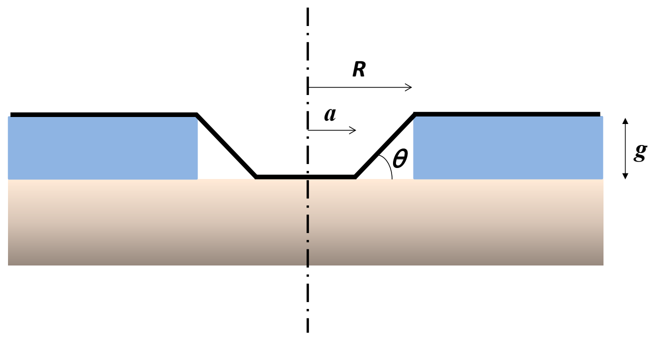

Figure S-3: Model of a stuck circular membrane of radius R, the stuck area is assumed to be circular with a radius a, and a cavity depth g. The tensed suspended part of the membrane forms an angle θ.

The geometric proportions mean the angle θ is relatively small, we can therefore approximate the slope by:

$$\theta = \sin(\theta) \approx \tan(\theta) = \frac{g}{R-a} = \left(\frac{g}{R}\right)\frac{1}{1-\sqrt{\eta}}. \tag{2}$$

where η is ratio of stuck-to-total area, g is the cavity depth, R is the drum's radius. We neglect radial displacement and assume only a vertical displacement $W(r)$ given as:

$$W(r) = \begin{cases} -g, & \text{for } 0 \leq r < a \\ \frac{g}{R-a}(r-a) - g, & \text{for } a \leq r \leq R \end{cases} \tag{3}$$

The radial strain induced by elongation can be obtained as [S-3]:

$$\epsilon_r = \frac{1}{2}\left(\frac{\partial W(r)}{\partial r}\right)^2, \tag{4}$$

The strain energy of the membrane is given by [S-3]:

$$U_s = \frac{\pi E_{2D}}{2}\int_0^R \epsilon_r^2 r dr = \frac{\pi E_{2D}}{2}\int_a^R \epsilon_r^2 r dr, \tag{5}$$

Since the adhesion area does not change upon pressure cycling, the stuck drum is in a stable force equilibrium between adhesion force and the tension. The adhesion force given as [S-4]:

$$F_{ad} = 2\pi a\Gamma, \tag{6}$$

where Γ is the adhesion energy in J/m^2. Inserting equation 3 in equations 4 and 5, and applying the static force equilibrium condition, i.e. $F_{strain} = \frac{dU_s}{da} = F_{ad}$, the adhesion energy can be expressed in terms of geometric parameters and E_{2D} as:

$$\Gamma = 16E_{2D}\left(\frac{g}{D}\right)^4 \frac{2+\sqrt{\eta}}{\sqrt{\eta}\left(1-\sqrt{\eta}\right)^4}. \tag{7}$$

4. Raman spectroscopy of suspended and collapsed drumheads.

A Renishaw in via system is used to scan a focused laser spot (λ = 514 nm) over the a suspended and a collapsed drumheads of 15 μm in diameter and 570 nm of cavity depth. We use the streaming feature to perform line scans of 25 μm in 360 s with steps of 600 nm at a laser power of 25 mW.

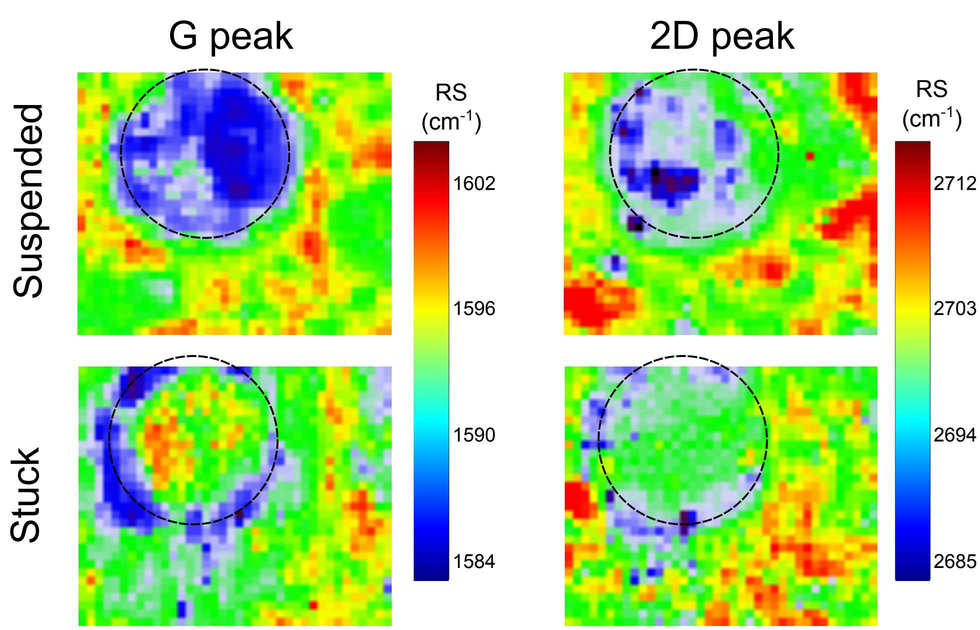

Figure S-4: G and 2D Raman peaks maps of a freestanding (top) and a collapsed drums (bottom) of 13 μm in diameter.

Figure S4 show the spatial maps of the G and 2D peaks of a freestanding (top) and a collapsed drums (bottom). These images not only indicate a high strain in the stuck drum (in the suspended areas), but also a higher strain in the anchoring area nearest to the drum compared to the same area of the suspended drum, thus indicating that some of the stress induced by stiction is being transferred to the graphene outside the drum.

5. Theoretical limit of large-diameter drums before collapse.

Equation 3 in the main text relates the deflection δ of a circular membrane under a pressure difference ΔP across it:

$$\Delta P = \frac{16T_0}{D^2}\delta + \frac{128\pi E_{2D}}{3D^4(1-\nu)A_T}\delta^3, \tag{8}$$

where T_0 is the pretension in the structure, E_{2D} is the 2D Young's modulus of the graphene membrane, $\nu = 0.16$ is the Poisson's ratio of graphene, and D is the membrane's diameter.

Assuming a perfectly impermeable membrane with $T_0 = 0.017$ N/m (Cartamil-Bueno et al, work in progress) under a pressure difference of 1 bar, we can find the minimum value of the Young's modulus to deflect the center of the circular membrane a distance equal to the depth of its cavity $\delta = g$. Figure S5 shows the colormap of the minimum Young's modulus for different cavity depths and diameters in the case of SLG (left) and DLG (right).

Given the fact that pristine graphene has a Young's modulus of 1 TPa and assuming that is the maximum value a CVD graphene can have, the theoretical model predicts a maximum diameter for a particular cavity depth beyond which the membrane would contact the bottom of the cavity and possibly collapse. For instance, all DLG membranes larger than 10 μm in diameter would contact the bottom of their cavities for cavity depths of 285 nm. The fact that some of the drums survive (Figure 3 in the main text) even though they are expected to touch the cavity bottom according to Figure S-5, might be caused by unsticking from the cavity bottom or by membrane pores that result in smaller values of ΔP.

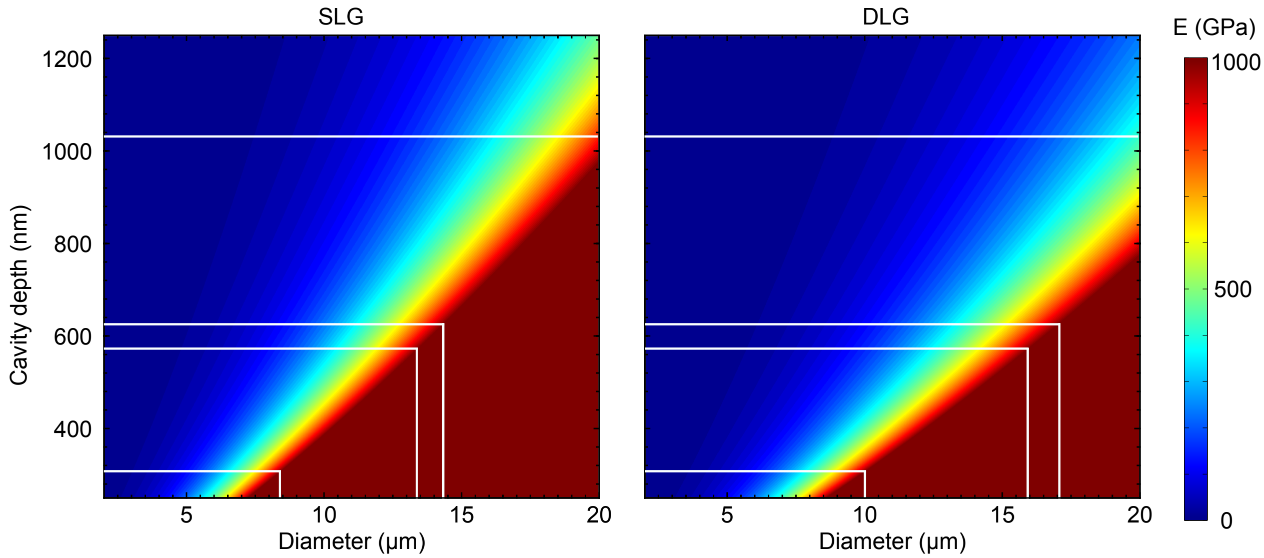

Figure S-5: Minimum Young's modulus of circular SLG (left) and DLG (right) membranes for different diameters and cavity depths for which a pressure difference of 1 bar would induce a deflection equal to the cavity depth.

6. Stuck drums and the diameter-dependence of their existence.

Figure S-6 shows an AFM image of the drumhead membrane shown in the inset of Figure 5 in the main text. Figure S-7 shows the ratio of stuck devices to the total number of devices as a function their diameter. Only samples with the four cavity depths indicated in the legend contain these stuck devices.

7. Complete dataset of yield for SLG and DLG samples.

The tables in .xls files collect all the yield data for the SLG (S8) and DLG samples (S9) used in this work.

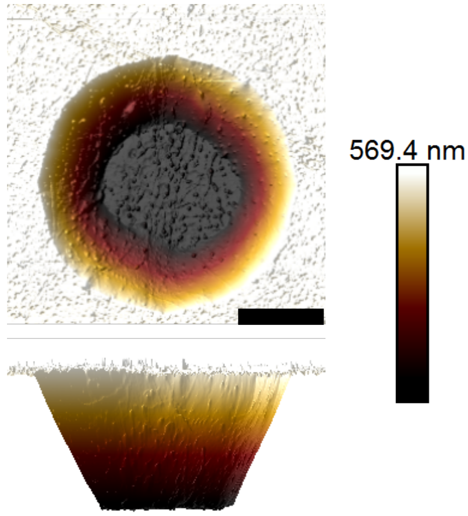

Figure S-6: AFM image of a stuck drum see from above (top) and cross section (bottom). Scale bar is 5 μm.

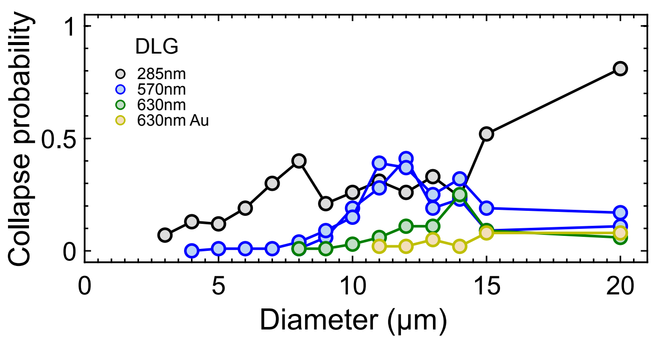

Figure S-7: Proportion of stuck drums as a function of their diameter.

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