# NANO-MECHANICAL CHARACTERIZATION OF FREELY-SUSPENDED TWO-DIMENSIONAL MATERIALS WITH ATOMIC FORCE MICROSCOPY

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## ABSTRACT
The surge of two-dimensional (2D) materials has taken the world by storm and became a new research hotspot as the characterization of nanoscale properties became a necessity. Lately, emphasis has been given to the synthesis of these materials and their heterostructures for mass production and integration in various applications, but the values of their properties are mostly theoretical and experimental data at the nanoscale are scarce. Therefore, in order to incorporate two-dimensional materials in the application of interest, one must first understand the full extent of their properties at the nanometer scale. One of the most powerful techniques for nanoscale characterization is Atomic Force Microscopy (AFM), which can be practiced even at atomic scale resolution. The plethora of its sub-modes can identify mechanical, electrical, magnetic, chemical and even vibrational properties at the nanometer scale, in conjunction with topography. The purpose of this study is to showcase the investigation of mechanical properties of 2D materials and their heterostructures by suspending them on top of patterned substrates, with the aid of AFM. This method permits the experimental assessment of nanoscale mechanical properties, such as breaking strength, Young's Modulus and interface/layer-by-layer interactions of heterostructures as well as the evaluation of the theoretical data and the corroboration of their significance.

## 1. INTRODUCTION
In the past years, the scientific community has expanded the study of 2D materials beyond electronic and optical properties, into the exploration of their mechanics. Substantial questions, such as how atomically thin materials respond to mechanical strain at the nanoscale, have researchers pondering since their discovery. The intrinsic mechanical properties of 2D materials exhibit large Young's modulus, low residual stress and spectacularly large breaking strength, to name a few [1].

In the recent years, diverse fabrication methods have flourished in order to isolate atomically thin 2D materials. The selection of the appropriate method strongly correlates on the application of interest, as different techniques yield different size, thickness and quality of the fabricated 2D crystals and hence different mechanical properties. Mechanical exfoliation, also referred to as micromechanical cleavage, has proven to be a simple yet powerful technique to obtain high-quality two-dimensional sheets by recurrently cleaving bulk layered materials [2]. The weak van der Waals interaction between the layers makes it possible to detach thin crystalline flakes by peeling off the surface of a bulk layered material. These flakes can be transferred to an arbitrary substrate by gently pressing the tape against the surface of the substrate and peeling it off slowly [3]. Although this method can produce high-quality flakes, its main drawback is the lack of control on the deposition step as the repeatability diminishes and the difficulty of a larger scale transition. Nevertheless, it has been shown that one can identify 2D flakes, and distinguish them from thicker counterparts, in a fast and reliable way by optical microscopy. Important aspect of this technique is that atomically thin crystals show a characteristic color when they are deposited on top of

certain substrates, due to a combination of interference color and optical absorption, which depends on the number of layers [4].

In order to study the mechanical properties of atomically thin materials, it's typically required to fabricate freely suspended samples. Three main approaches are employed to fabricate these suspended structures: (i) direct exfoliation (flakes randomly distributed) onto pre-patterned substrates with holes/trenches [5], [6], (ii) etching the substrate underneath the flakes [7] or (iii) depositing the flakes directly onto a specific cavity on the substrate using a transfer technique [8]. The most widely used approach for mechanical properties examination is obtained from force curves as a function of the indentation depth at the center of a freely-suspended membrane (**figure 1**). The analysis models take into consideration the existing pre-tension and the bending rigidity of the membrane, as well as the Young's modulus and the hardness of the material [9].

In this study, graphene flakes were directly mechanically exfoliated onto patterned $SiO_2$/Si substrates and were subjected to nanoindentation experiments. Previously, the flakes were identified for their quality and quantity with optical microscopy, Raman spectroscopy and Atomic Force Microscopy. The freely-suspended membranes, allowed us to attain Young's modulus measurements, without the contribution of the substrate, which were in close accordance with the theoretical predictions.

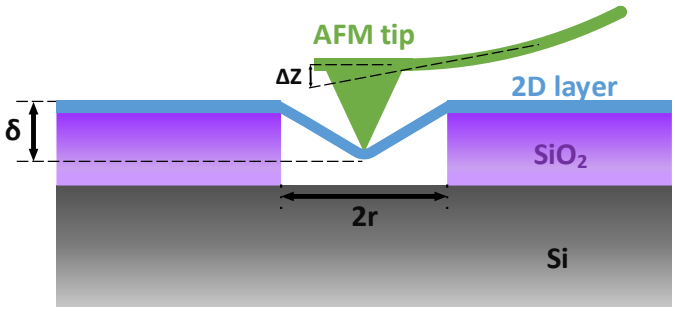



***Figure 1.*** *Typical nanoindentation experiment.*

## 2. EXPERIMENTAL SECTION

### *2.1. Materials preparation*

$SiO_2$/Si substrates with 90 nm oxide thickness were patterned with holes by optical lithography. Pore diameter and depth were 2.5 μm and 1.5 μm respectively. Graphene flakes were prepared by mechanical exfoliation of HOPG (Highly Ordered Pyrolytic Graphite) with the scoth tape method, and were directly deposited on top of the aforementioned $SiO_2$/Si substrates.

### *2.2. Optical and Morphological characterization*

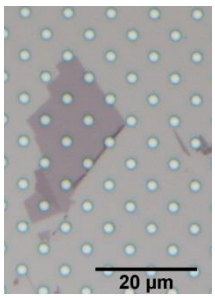
Optical identification of the 2D flakes was performed by an optical microscope (Nikon) with a x50 objective lens. Raman spectra (InVia Renishaw) were excited by a solid state laser operating at 514 nm. Laser power was kept at 1.2 mW on the sample in order to avoid laser-induced local overheating. A ×100 objective with numerical aperture of 0.95 was used for the focus of the laser. AFM measurements (Bruker Dimension Icon) were carried out using a Bruker multimode 9.13. The scanning modes used were: (1) quantitative nanomechanical mapping (QNM), where the cantilever periodically indents the samples and mechanical data is extracted from the measured force curves, (2) PeakForce Tapping mode for the acquisition of topography without altering the surface characteristics. All measurements were carried out with a DDESP-V2 tip (stiffness 80 N/m, frequency ~450 kHz), where deflection sensitivity was calibrated using a sapphire standard, and elastic modulus was then calibrated on a polystyrene film standard of known elastic modulus (2.7 GPa).

*2.3. Nanoindentation experiments*

Suspended graphene membranes were first scanned in PeakForce Tapping mode to locate the area of interest. Subsequently, Point and Shoot mode was used at the center of the membrane (within 10% error) to obtain individual force curves. A range of force values was used as a trigger (0.5 μN – 3 μN) for the acquisition of multiple datasheets. All data were analyzed with Nanoscope Analysis software.

## 3. RESULTS AND DISCUSSION

3.1. Optical identification of exfoliated flakes




Graphene flakes were directly mechanically exfoliated on top of patterned $SiO_2$/Si substrates. The $SiO_2$ layer thickness was 90 nm, which has been reported as the optimal thickness for graphene optical identification, due to the correlation of the number of layers with optical contrast [4]. Optical image of the examined flake is shown in **figure 2**. For more precise assessment, Raman spectroscopy and Atomic Force Microscopy were employed. The results are shown in the following sections.

***Figure 2.*** *Mechanically exfoliated graphene flake.*

3.2. Quality assessment with Raman spectroscopy and Atomic Force Microscopy

The exact nature of the flake was assessed by the corresponding Raman spectra of the graphene flake. More specifically, Raman mapping of the deposited film on top of the patterned $SiO_2$/Si substrates was acquired. As it is clearly presented in **figure 3**, the average ratio between the $I_{2D}/I_G$ was found to be around 1. Furthermore, the FWHM of 2D band is approximately 55 $cm^{-1}$ which confirms that the deposited flake is a bi-layer graphene [10]. Moreover, the position of the 2D band around the holes at 2696 $cm^{-1}$, proves that graphene has no residual stress due to micromechanical cleavage. Inside the holes, the 2D peak position shows a blue shift towards lower wavenumbers which means that graphene is under a mild tensile strain.

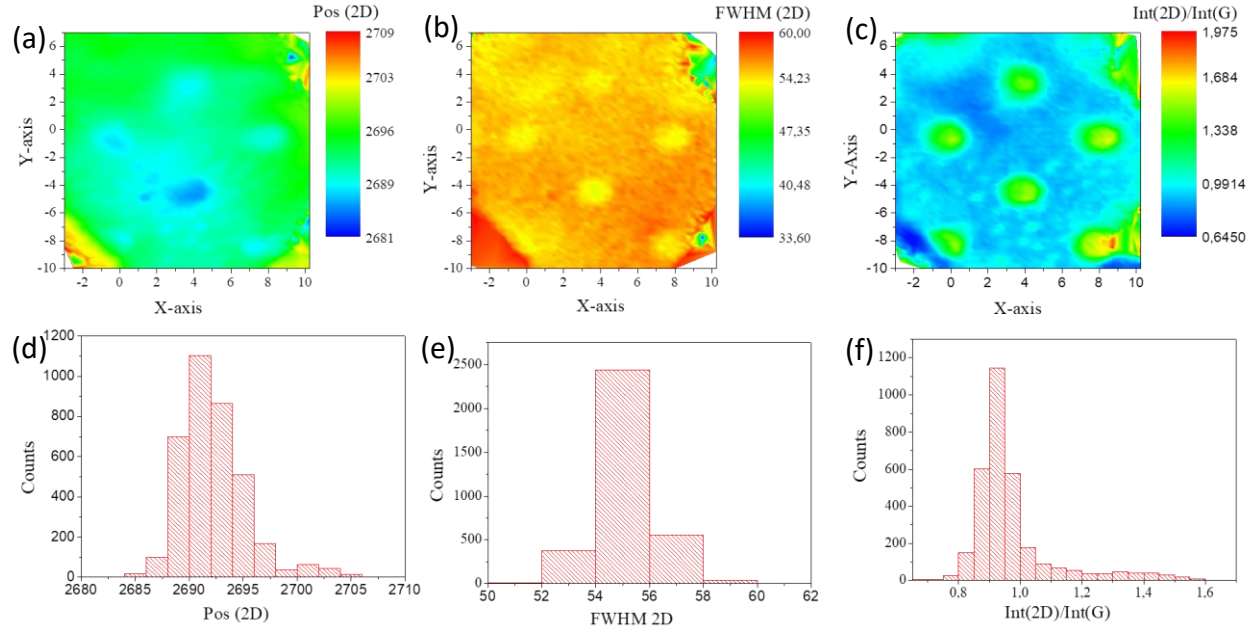



***Figure 3.*** *Raman mapping of (a) 2D peak position, (b) 2D peak FWHM, (c) Int(2D)/Int(G). Corresponding histograms of (d) 2D peak, (e) 2D FWHM, (f) Int(2D)/Int(G)*

PeakForce Tapping mode gave us the topography image of the selected experiment area (**Fig 4**). As shown, the membrane is tautly stretched across the hole and its also revealed that graphene adheres to the vertical walls for ~20 nm, due to van der Waals interactions with the substrate. The thickness of graphene was found to be ~0.9 nm which corresponds to a bilayer, as also confirmed by Raman spectroscopy.

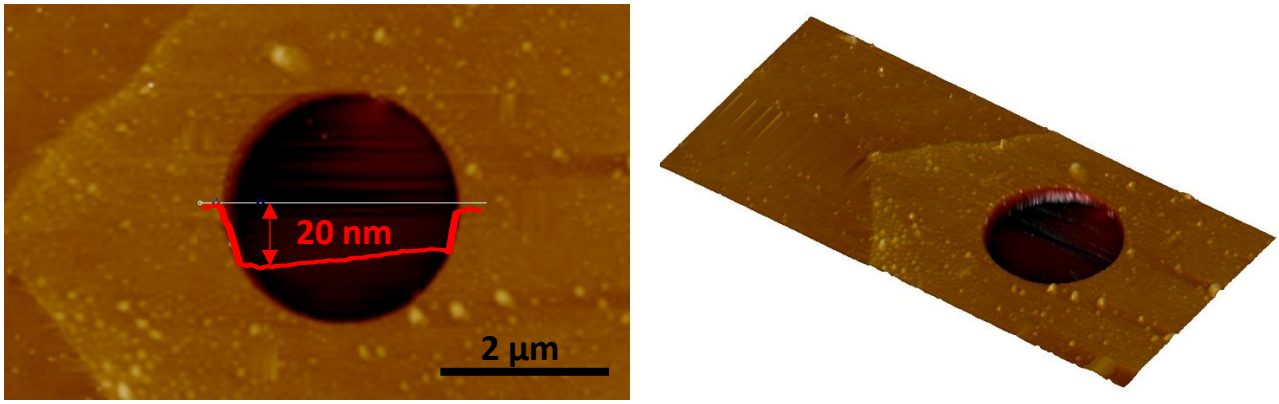



***Figure 4.*** *AFM topography scan of the selected experiment area.*

3.3. Nano-mechanical characterization

The mechanical tests were performed at a constant deformation rate, followed by load reversal. This cycle was repeated several times and the data showed no hysteresis, which demonstrated the elastic behavior of the film and confirmed that the graphene film did not slip around the edges of the well. The force-displacement measurements were highly repeatable, even for different displacement rates, and the yielded values of the elastic modulus were statistically indistinguishable. A typical loading/unloading curve is presented in **figure 5(b)**. Once the data for elastic properties of the film were recorded, it was once again indented, but this time to failure. The force-displacement data were processed to determine the elastic properties and breaking stress of the graphene membrane.

Due to graphene being a 2D material, its strain energy density is normalized by the area of the graphene sheet rather than by the volume. Therefore, its behavior under tensile loading is properly described by a 2D stress $\sigma_{2D}$ and elastic constant $E_{2D}$ with units of force/length. For comparison purposes to bulk graphite, these quantities can be divided by the interlayer spacing in graphite (h = 0.335 nm) in order to obtain the corresponding 3D parameters. The relationship between the applied force at the center of the flake and the resulting deformation of the suspended nanosheet is:

$$F = \left[\frac{4\pi E}{3(1-\nu^2)}\left(\frac{t^3}{a^2}\right)\right]\delta + (\pi T)\delta + \left(\frac{q^3 E t}{a^2}\right)\delta^3, \qquad (1)$$

where F is the applied force, δ is the sheet displacement, E and ν are Young's modulus and the Poisson ratio (ν = 0.125) [11], t is the thickness of the nanosheet, a is its radius, T its pre-tension and $q = 1/(1.05 - 0.15\nu - 0.16\nu^2)$ is a dimensionless constant. The first term in Equation 1 corresponds to the mechanical behavior of a plate with a certain bending rigidity [12], [13]. The second term represents the mechanical behavior of a stretched membrane [6]. Finally, the third term takes into account the stiffening of the layer during the force load cycle which makes F(δ) nonlinear [12]. The cubic thickness dependence ($t^3$) of the bending rigidity makes it the most relevant term for the thicker sheets. On the other hand, the static and deformation-induced tension terms are the most significant ones for ultrathin sheets, explaining the observed crossover from non-linear to linear F(δ). The effect of shearing stresses, on planes parallel to the surface of

the plate, can be neglected because of the low plate thickness to plate radius ratio (t/a). The maximum stress for a clamped, linear elastic, circular membrane under a spherical indenter as a function of applied load is given by:

$$\sigma_m^{2D} = \left(\frac{FE^{2D}}{4\pi R}\right)^{\frac{1}{2}}, \qquad (2)$$

where $\sigma_m^{2D}$ is the maximum stress at the center of the membrane.

**Figure 5** presents the examined area for nanoindentation experiments along with a representative force vs. deformation curve measured at the center of the suspended membrane. For data analysis, the unloading curve was chosen in order to avoid any contribution of van der Waals forces. The elastic modulus and pre-tension of the suspended film was deducted by fitting the data to equation (1). The mean values were $E_{2D}$=1050 $Nm^{-1}$ and $\sigma_{2D}$= 0.28 $Nm^{-1}$, which translate to E=1.1 TPa ± 0.1 TPa and σ=0.31 GPa ± 0.03 GPa respectively.

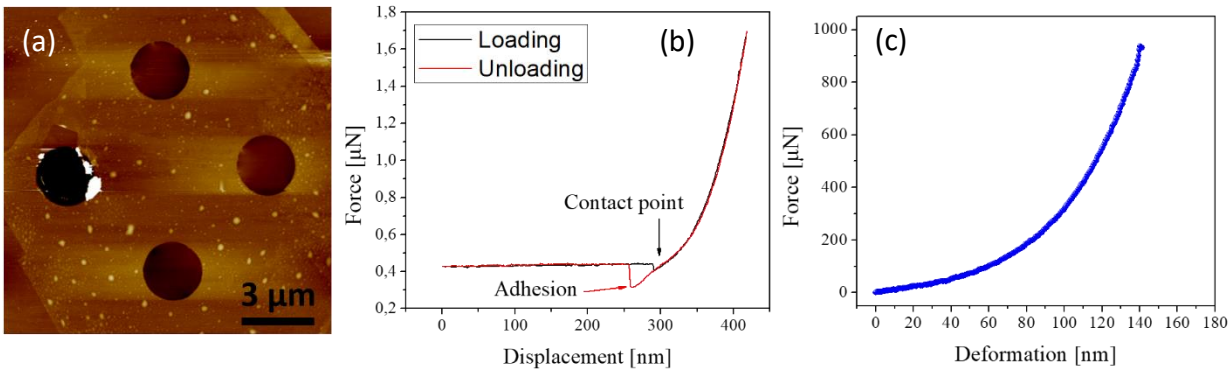



***Figure 5.*** *(a) Topography of the examined area, (b) Typical loading/unloading curve, (c) representative force vs. deformation curve for data analysis.*

The topography image after the breaking of the membrane is shown in **figure 6**. The breaking strength of graphene was found by fitting the data to equation (2). By taking into consideration the tip radius (100 nm) and the elastic modulus found previously (1050 $Nm^{-1}$) and the force at breaking point (10.82 μN) we get a breaking strength of $\sigma_m$=102 GPa ± 10 GPa.

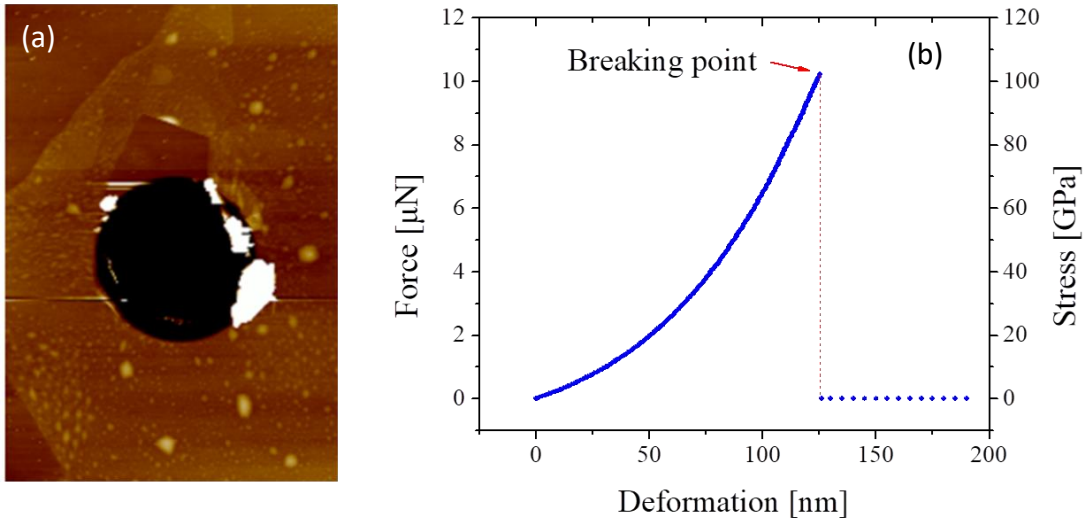



***Figure 6.*** *(a) Topography of fractured graphene membrane, (b) force and stress vs. deformation curve.*

## 4. CONCLUSIONS

In conclusion, we demonstrated an effective method to gather nanoscale mechanical properties without the contribution of a substrate. In order to test the method's viability, bilayer graphene was mechanically exfoliated on top of patterned $SiO_2$/Si substrates and was indented with an AFM tip. The force-displacement curves were fitted to the derived model for free-standing circular drum membranes. The results were a perfect match with the theoretical values of graphene's Young modulus of approximately 1 TPa and breaking strength of 102 GPa. The undeniable benefit of this technique is that it can measure the true intrinsic properties of ultrathin membranes like 2D materials and most importantly, their heterostructures. This novel process can be applied to a multitude of materials and could pave the way for standardizing the metrology of nanoscale characterization of mechanical properties.

## ACKNOWLEDGEMENTS

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