

# Evolution of Mechanical Properties from Graphene to Graphene Oxide Studied by AFM Nanoindentation

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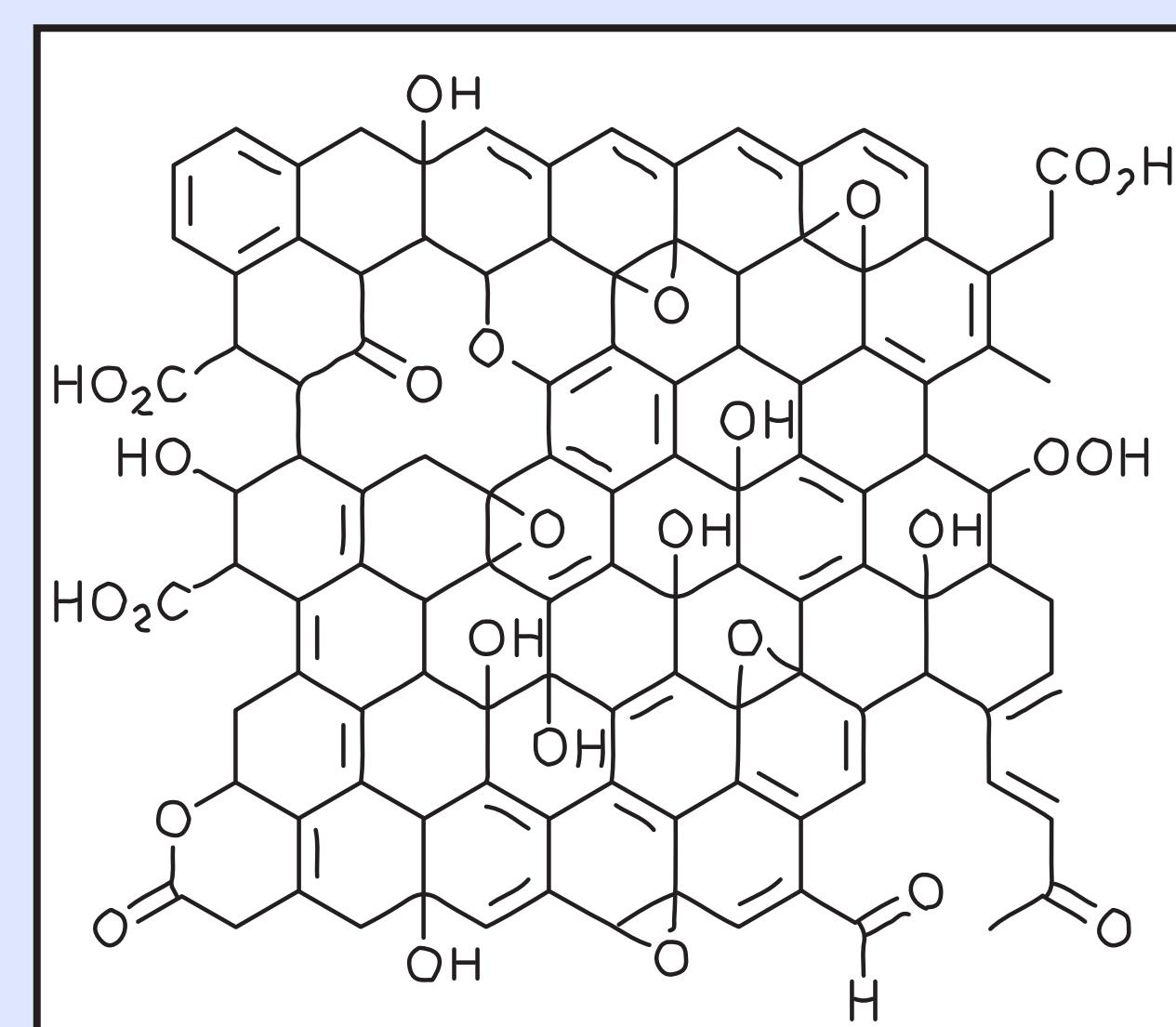
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## Introduction

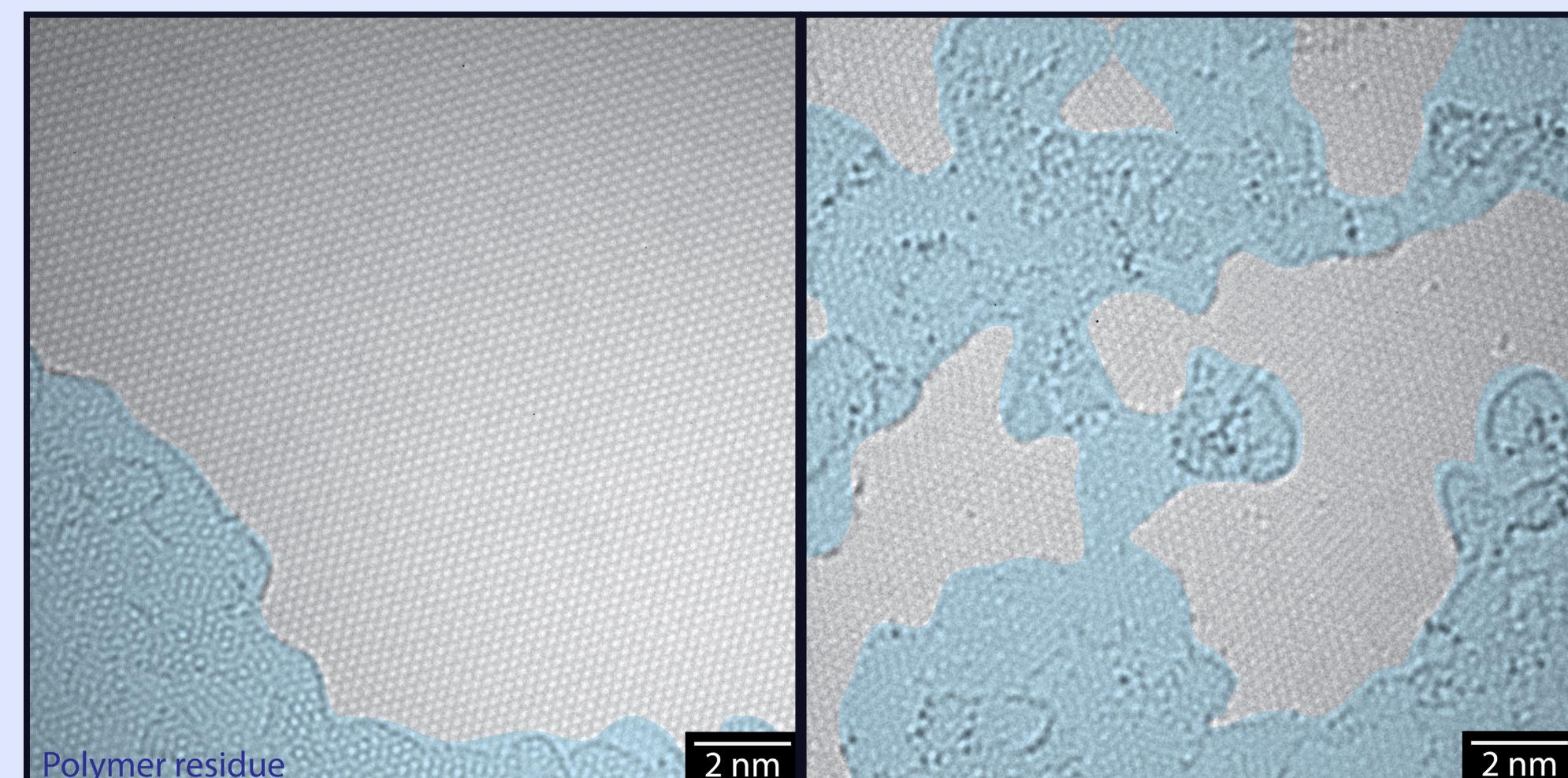
- Graphene is an interesting material due to its 2-dimensional nature and its remarkable properties.
  - It is noted for its particularly high strength and stiffness.
- Graphene oxide (GO) is a derivative of graphene that features many oxygen based groups, mainly epoxy and hydroxyl groups.
- Graphene can be functionalised with oxygen for a controlled change towards graphene oxide.
- The properties of graphene and graphene oxide are different, and it is important to know and understand these properties if they are to be harnessed.
- Here we investigate the variation in mechanical properties with functionalisation from graphene to graphene oxide.



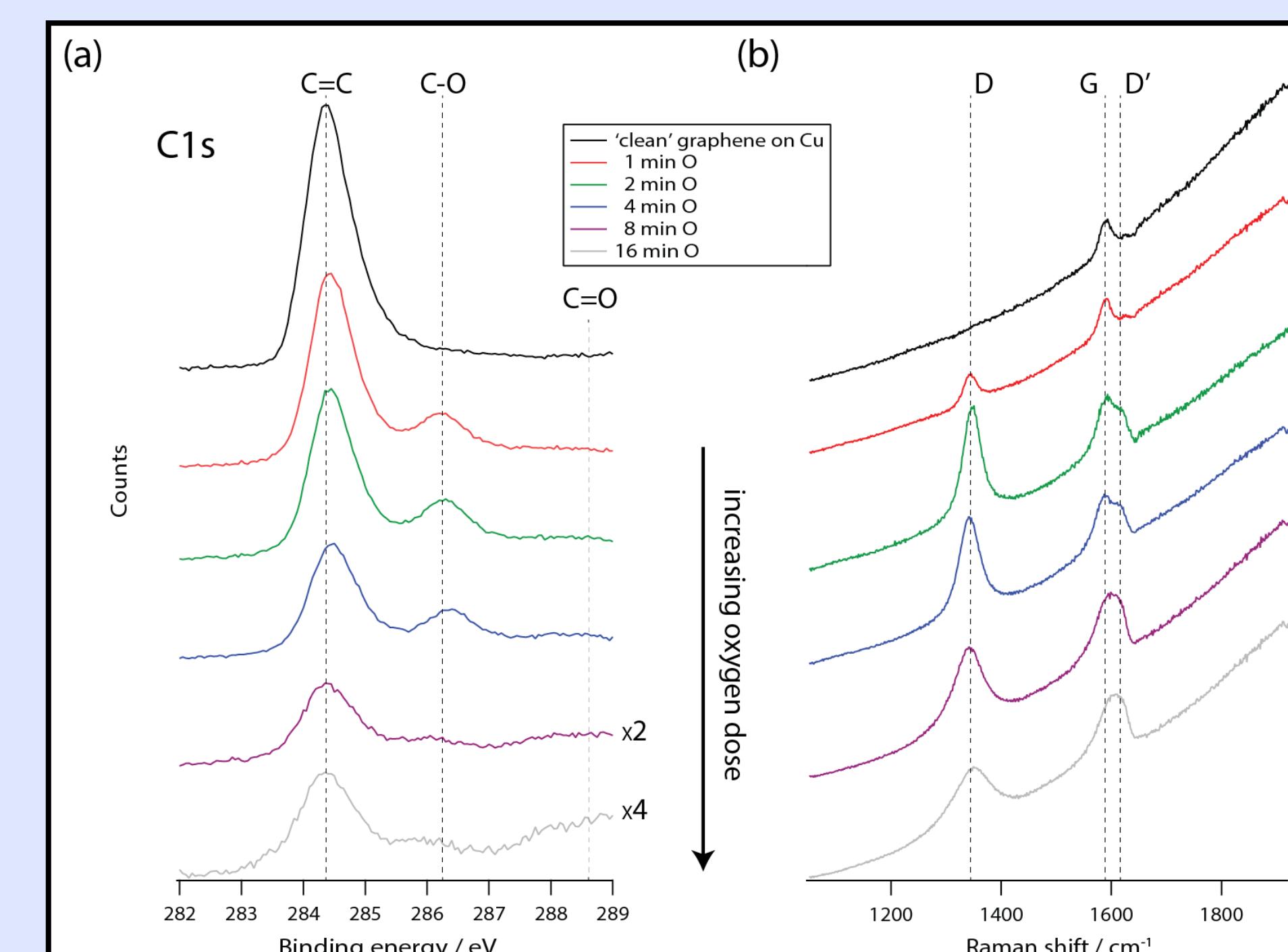
The Lierf-Klinowski graphene oxide structural model.<sup>1</sup> There are many oxygen groups, topological defects and vacancies present within the graphene structure.

## Oxygen Functionalisation

- Graphene is grown using chemical vapour deposition (CVD) on copper foil.
  - Transfer is achieved by spin coating a polymer layer on top for support and etching away the copper. The polymer is then removed by dissolution it and sometimes heating the sample.
- Graphene is exposed to atomic oxygen under UHV conditions for varying lengths of time to produce different levels of oxygen functionalisation.
- GO is also produced by conventional wet chemical approaches, and is applied to samples by drop casting a liquid suspension.
- XPS and Raman of oxygen functionalised graphene shows an increasing presence of oxygen groups and disorder.
- TEM images show that graphene is produced in a near pristine state, but defects are introduced during functionalisation.



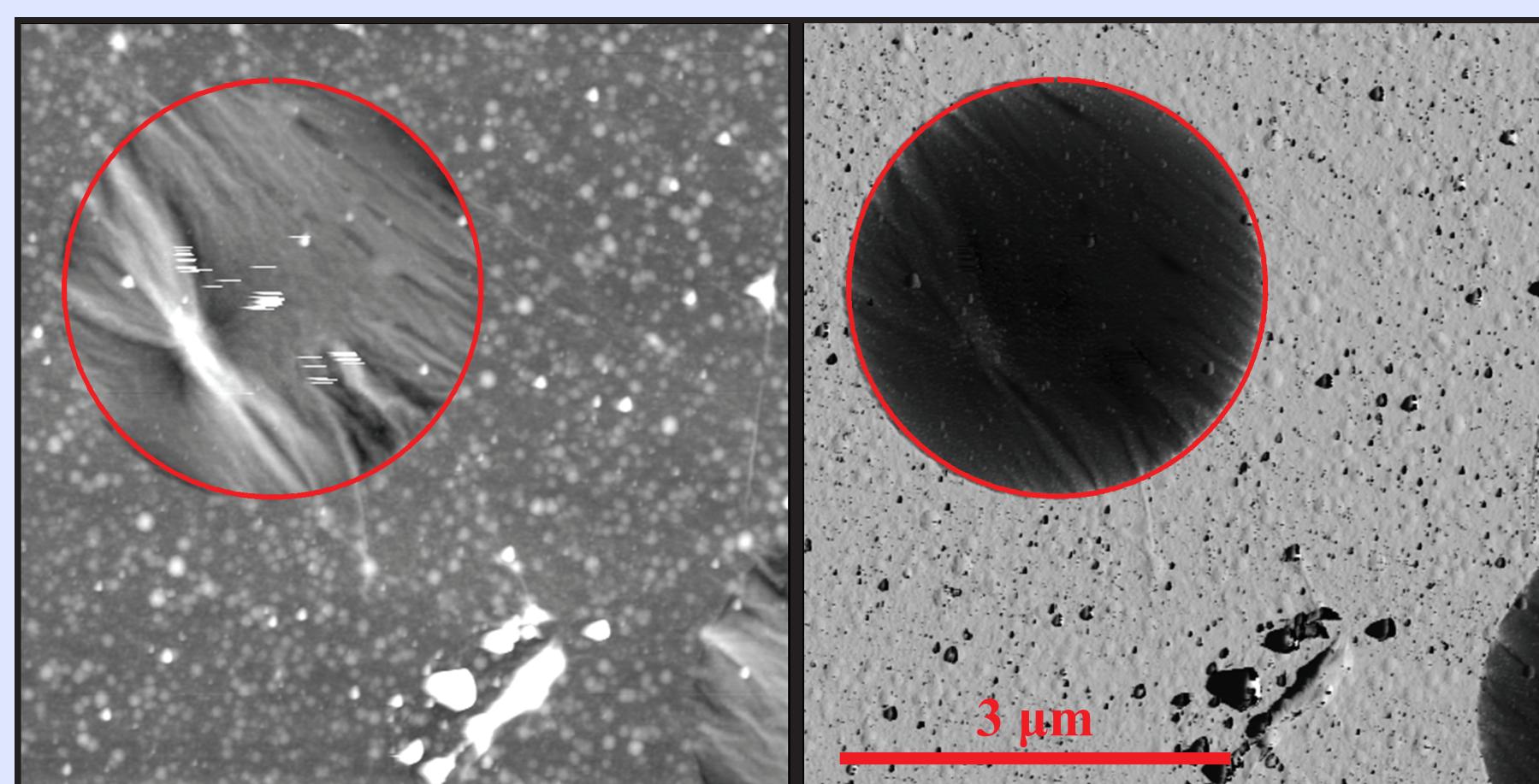
TEM images of CVD grown graphene (left), graphene after 6 minutes of oxygen dosing (middle) and as produced GO (right). The graphene shows a large uniform area, whereas the oxygen dosed sample has many defects present and the GO is less uniform again.



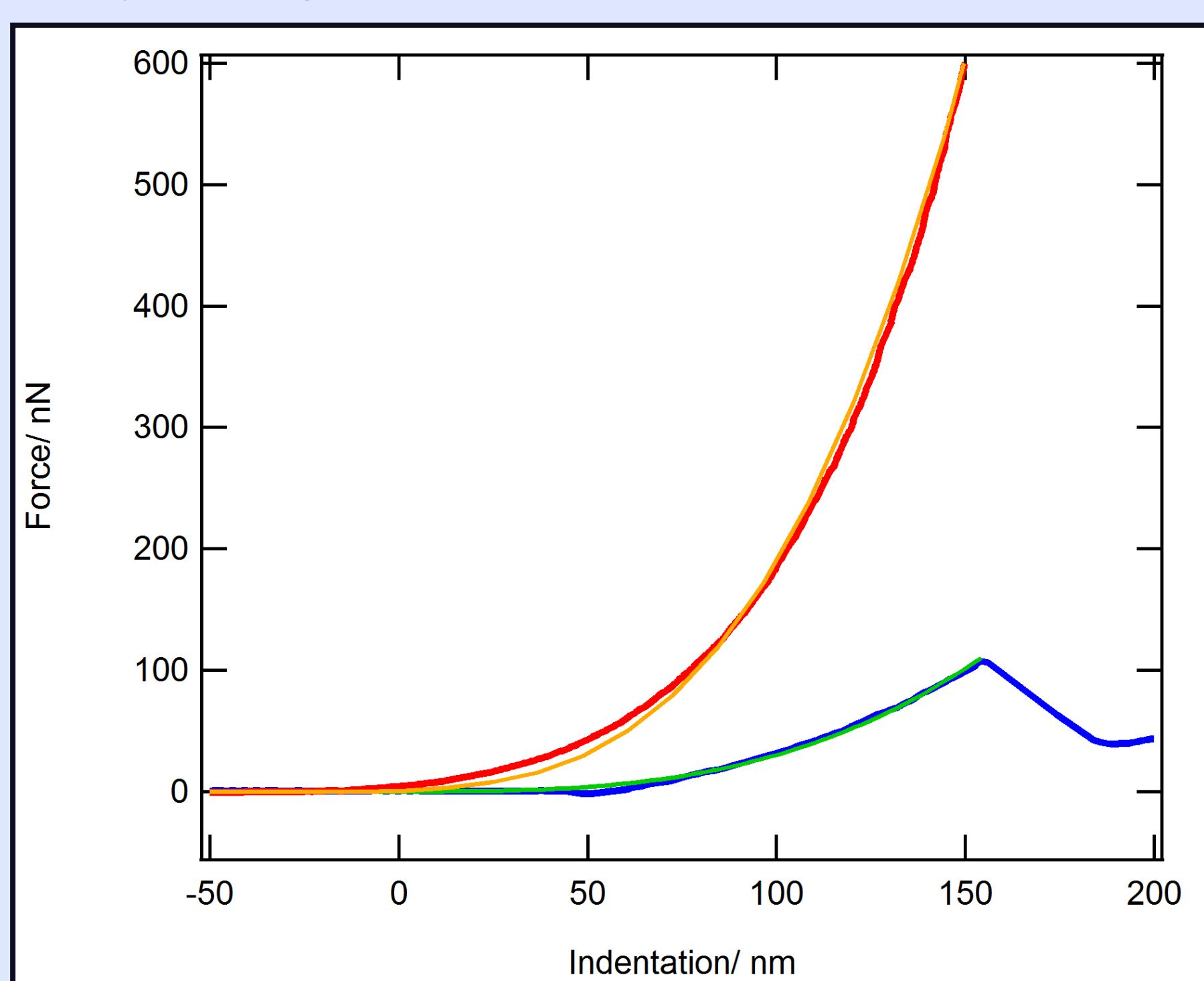
(a) XPS and (b) Raman spectra of graphene with increasing amounts of oxygen functionalisation. The XPS C=C peak is reduced and the C=O and C-O peaks start appearing, showing a shift from graphene to GO. The D peak in the Raman indicates disorder, increasing with more functionalisation.

## Mechanical Properties

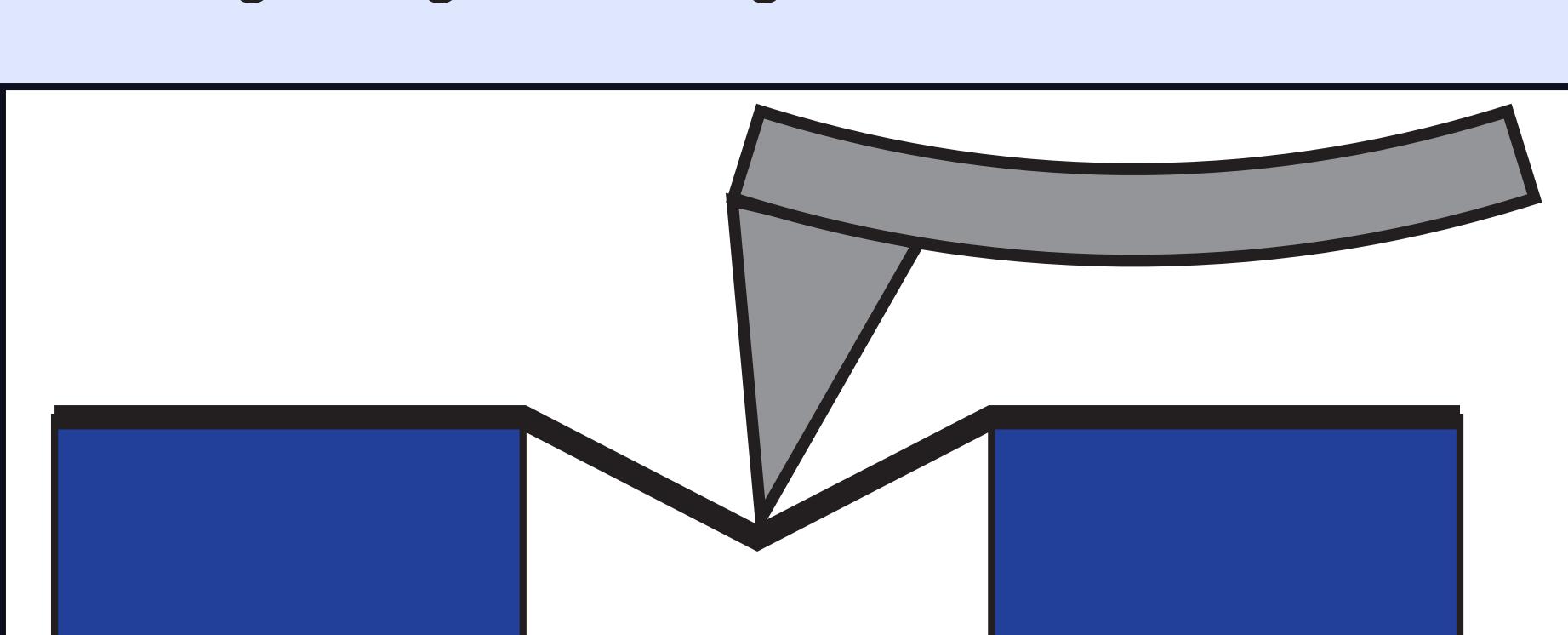
- Samples are transferred to a SiN grid which has an array of evenly spaced holes.
- Tapping mode scans of the membrane covered holes can be used to identify their location, allowing for large quantities of data to be acquired automatically.
- Force curves are performed in the centre of the holes, giving a 3<sup>rd</sup> order polynomial force vs indentation curve.
  - The coefficient of the 3<sup>rd</sup> power combined with the radius of the hole gives the 2D elastic modulus ( $E^{2D}$ ).
  - $E^{2D}$  can be converted to an effective Young's modulus by dividing by the material thickness (0.335 nm for graphene).
- Sharp drops are seen in the force curves, indicating when the film has broken.
  - Breaking strength depends on tip radius, but differences between similar tips and damage to the tips over time did not have a major impact.
- GO and oxygen dosed graphene all have significantly lower elastic moduli and breaking strengths compared to pristine graphene.
- Heated graphene has a lower elastic modulus, but breaking strength is still high.



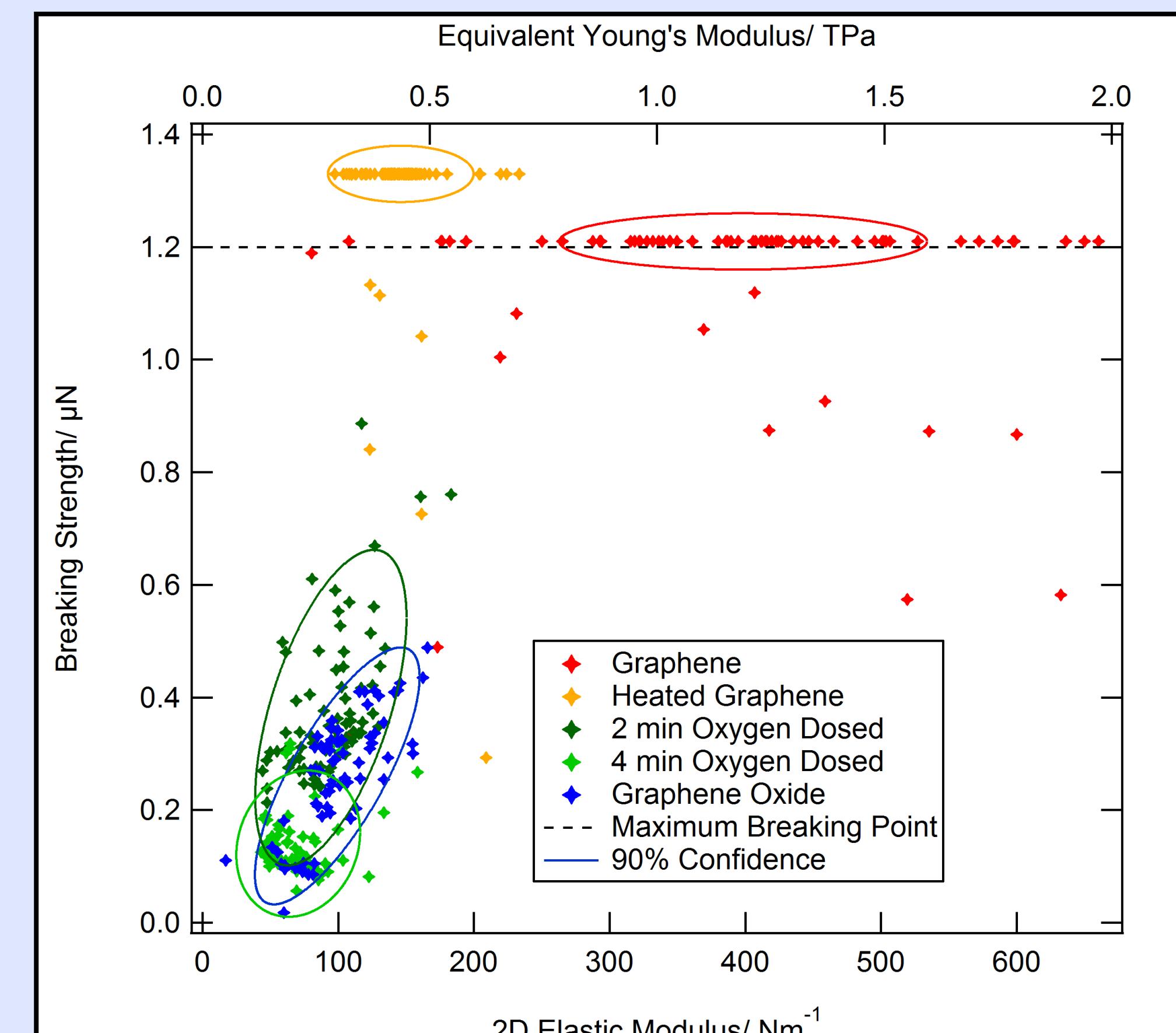
Height (left, 30 nm full scale) and phase (right, 65° full scale) tapping mode AFM images of a suspended graphene sheet. The high contrast in the phase image can be used to locate the hole (red circle).



Force curves for a graphene covered hole (red) and a GO covered hole (blue) and their respective fits (orange and green). The lower stiffness of the GO results in a much shallower curve. The measured values for  $E^{2D}$  are 450 N/m and 80 N/m respectively, corresponding to equivalent Young's Moduli of 1.3 TPa and 240 GPa. The GO is also seen breaking at 100 nN, the graphene didn't break with a maximum force of 1.2 μN.



Cross section of the AFM tip indenting a suspended sheet.



Collection of results from experiments on a range of graphene based materials. Breaking strengths above the dashed line are for sheets that did not break and the given value is the maximum force applied. Ellipses represent the 90% confidence intervals for the data, except for the graphene and heated graphene, where the breaking strength is not considered.

Average values from these are given in the table below, along with their standard deviation.

	Equiv. Young's Modulus (GPa)	Breaking Strength (nN)	Correlation Coefficient
Graphene	$1200 \pm 400$	>1200	N/A
Heated Graphene	$440 \pm 70$	>1300	N/A
2 min Oxygen	$280 \pm 80$	$380 \pm 130$	0.57
4 min Oxygen	$219 \pm 60$	$140 \pm 60$	0.15
Graphene Oxide	$300 \pm 80$	$260 \pm 110$	0.77

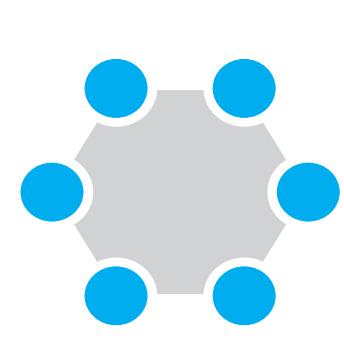
## Conclusions

- Controlled oxidation by atomic sources shows that functionalization proceeds first by the attachment of oxygen functional groups, which then irreversibly create defects (vacancies and vacancy clusters) in the graphene lattice.
  - These extended topological defects are present in graphene oxide
- Investigation of the mechanical properties shows that functionalization results in two effects: a decrease in stiffness by a factor of ~5 for graphene oxide, and a decrease in breaking strength by more than an order of magnitude.
  - The decrease in breaking strength is clearly correlated to the presence of extended topological defects.

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## References/Further Reading

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