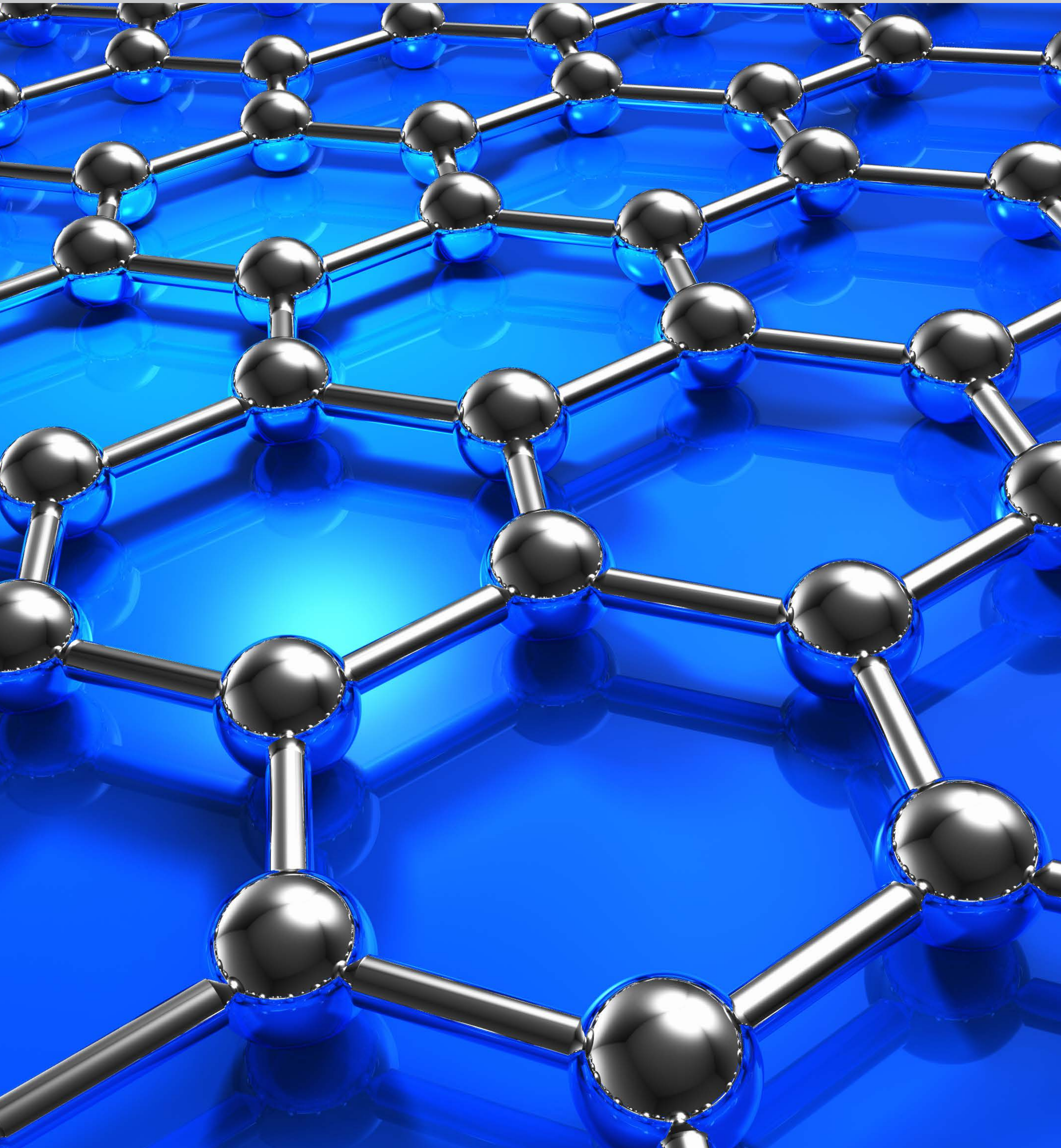
Raman measurements on graphene



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Renishaw's inVia confocal Raman microscope is an ideal tool for studying graphene. It is widely used for graphene research worldwide, and its results appear in many journal articles (inVia featured in over 1300 graphene papers in 2013 alone).

This document details the key measurements you can make on graphene with an inVia Raman microscope.

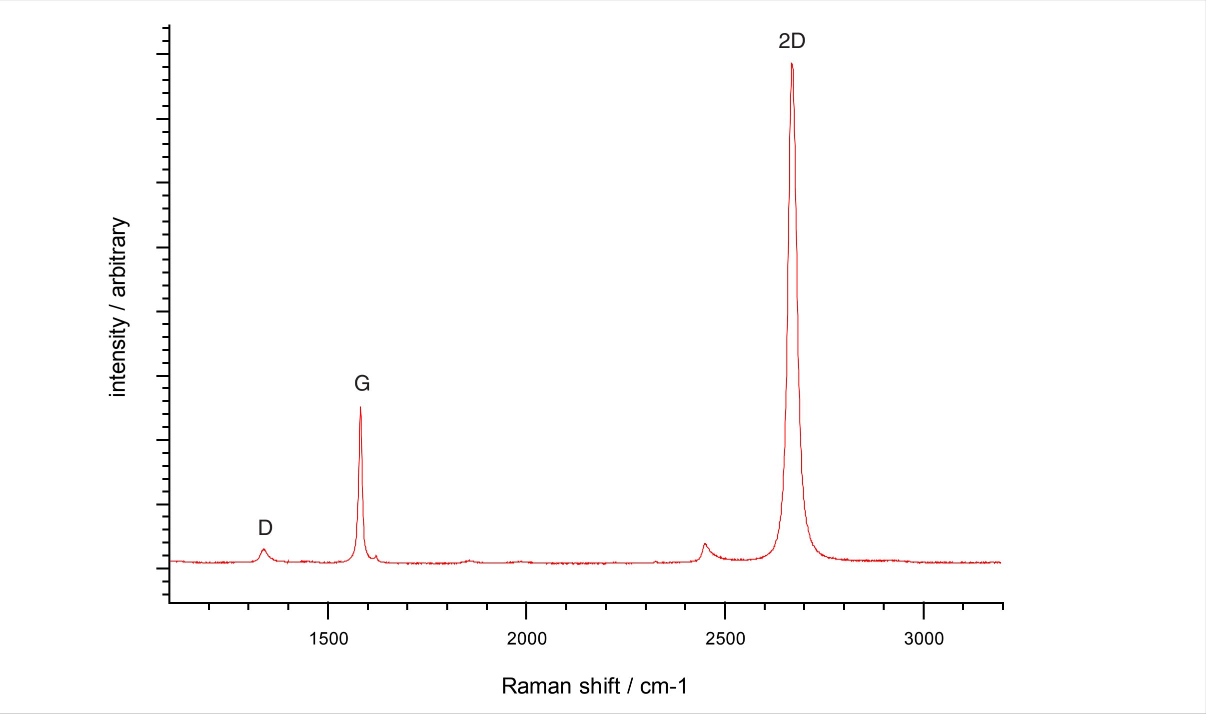
Contents

The Renishaw inVia confocal Raman microscope

1 Identify graphene

The high specificity of inVia enables graphene to be easily differentiated from other materials, including carbon allotropes such as carbon nanotube and diamond.

Raman spectroscopy was used to measure the spectrum of single-layer graphene on $Si0_2$/Si



Raman spectrum of single-layer graphene.

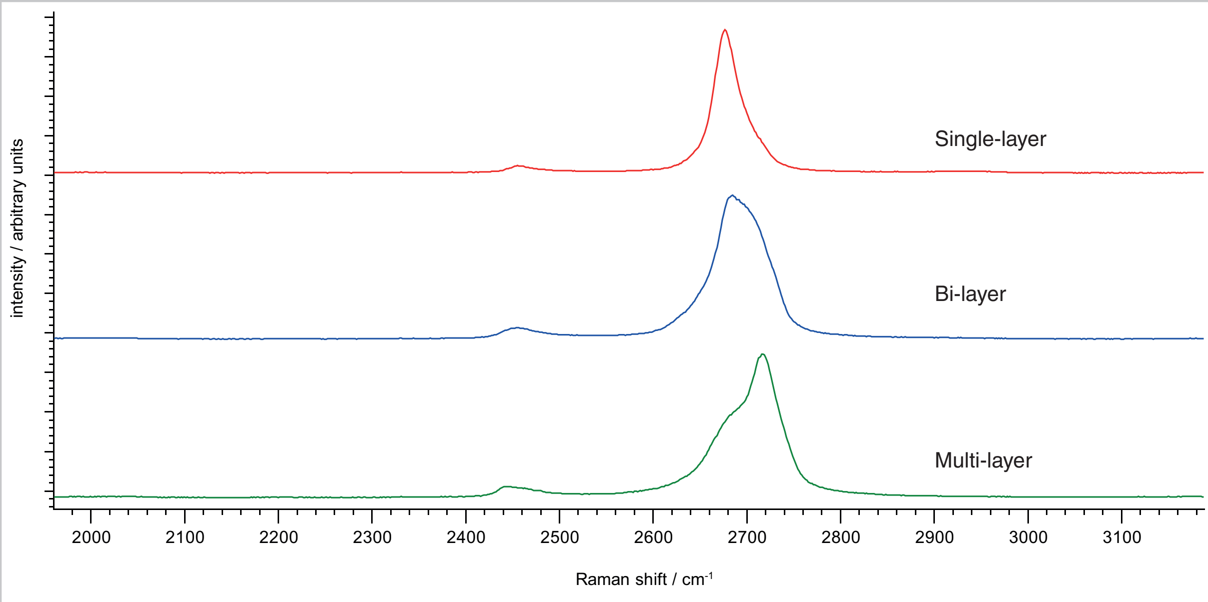
Experimental conditions

Instrument model	inVia confocal Raman microscope with standard edge filters
Excitation	532 nm laser
Objective	100× N Plan
Grating	2400 l/mm
Measurement type	Synchroscan
Acquisition time	10 s

2 Determine the thickness of mechanically exfoliated graphene

Easily and quickly identify the thickness of graphene created from the mechanical exfoliation of graphite.

The width and shape of the graphene 2D band depends on the number of graphene layers, making it easy to differentiate between single-, bi- and multi-layer regions.



Raman spectra from different numbers of graphene layers

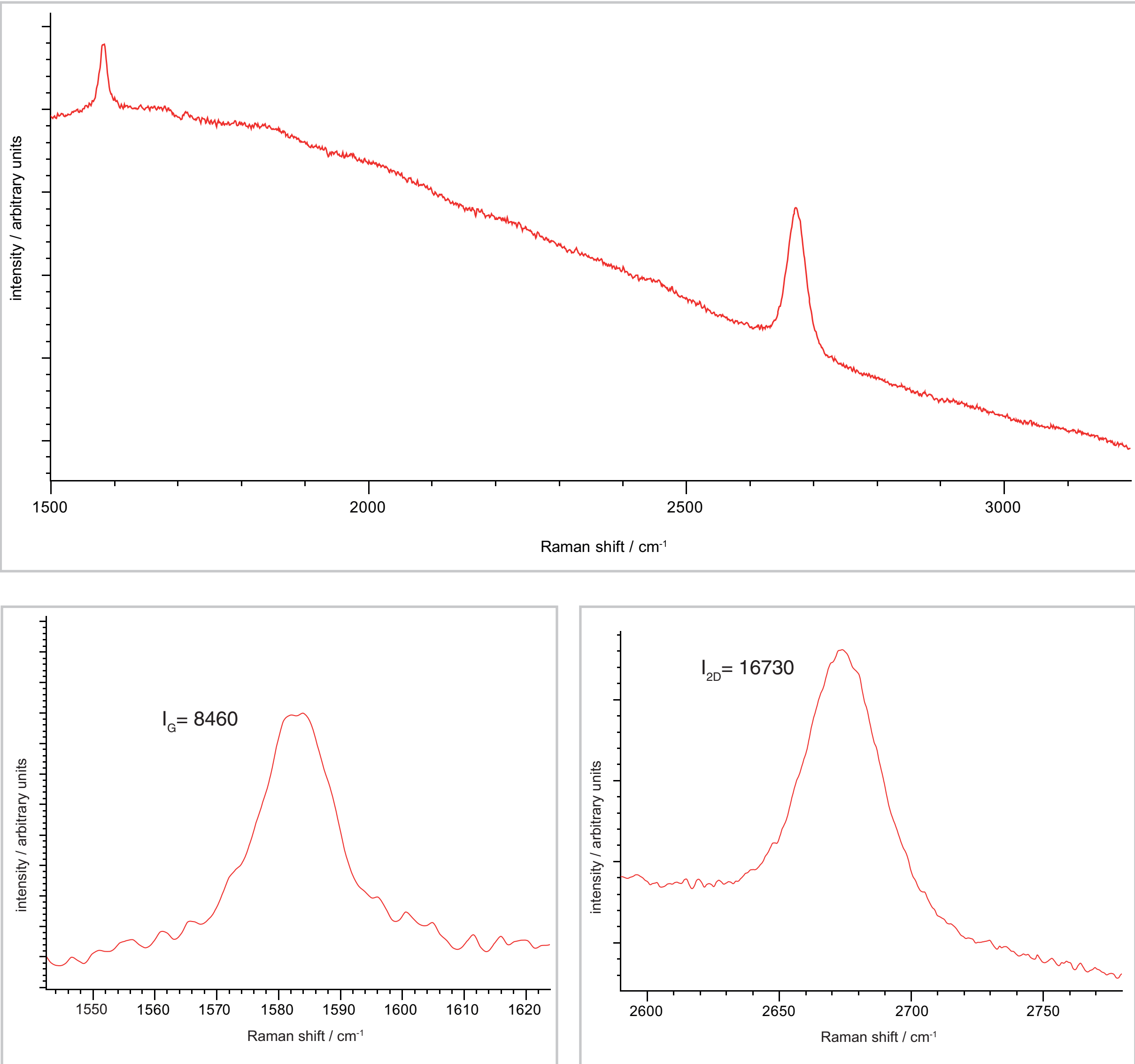
Experimental conditions

Instrument model	inVia confocal Raman microscope
Excitation	532 nm laser
Objective	100× N Plan
Grating	1800 l/mm
Measurement type	Static scan
Acquisition time	10 s

3 Determine the thickness of CVD graphene

Easily and quickly identify the thickness of CVD graphene.

The intensity ratio between the 2D and G peaks, I_{2D}/I_G, indicates the number of layers present in CVD graphene. If I_{2D}/I_G >2 then a sample is single-layer graphene, if 1< I_{2D}/I_G <2 then bi-layer graphene is present, and if I_{2D}/I_G <1 then 3 or more layers are present (see Murdock *et al*, *ACS Nano*, **2013**, 7 (2), pp 1351–1359).



Raman spectrum of bi-layer graphene grown by CVD on a copper substrate. $I_{2D}/I_G = 1.98$.

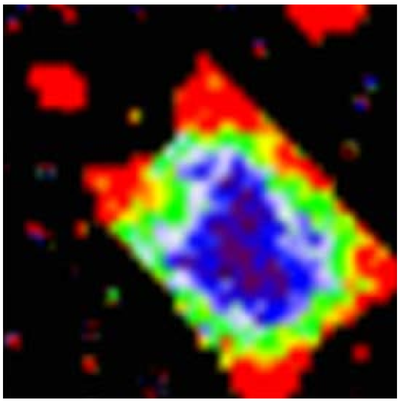
Experimental conditions

Instrument model	inVia confocal Raman microscope
Excitation	532 nm laser
Objective	100× N Plan
Grating	2400 l/mm
Measurement type	Static scan
Acquisition time	4 s

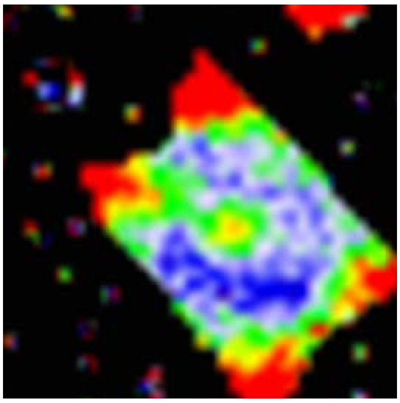
4 Image strain in graphene

Visualise strain and stress in graphene samples by imaging the G and 2D bands, which change position as a result of strain.

The Raman images below show a CVD graphene flake grown on copper and illustrate the shifts in frequency of the G and 2D bands. By analysing the shifts you can determine stresses. Here, compressive stresses are revealed at the edges of the flake where growth has been occurring. More details on this work can be found in Murdock *et al*, *ACS Nano*, **2013**, 7 (2), pp 1351–1359.



Raman image showing the frequency of the G-band



Raman image showing the frequency of the 2D-band

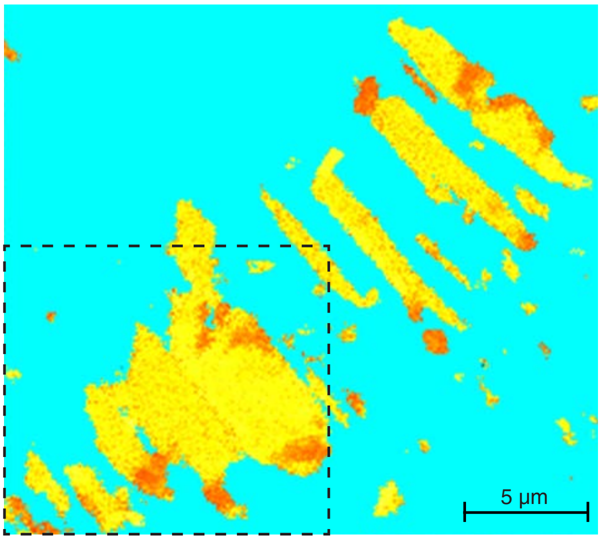
Experimental conditions

Instrument model	inVia confocal Raman microscope
Excitation	532 nm laser
Objective	100× N Plan
Grating	2400 l/mm
Measurement type	StreamLineHR™
Measurement area	7.2 µm × 7.6 µm (0.2 µm step size)
Number of spectra	1,443
Measurement time	10 s

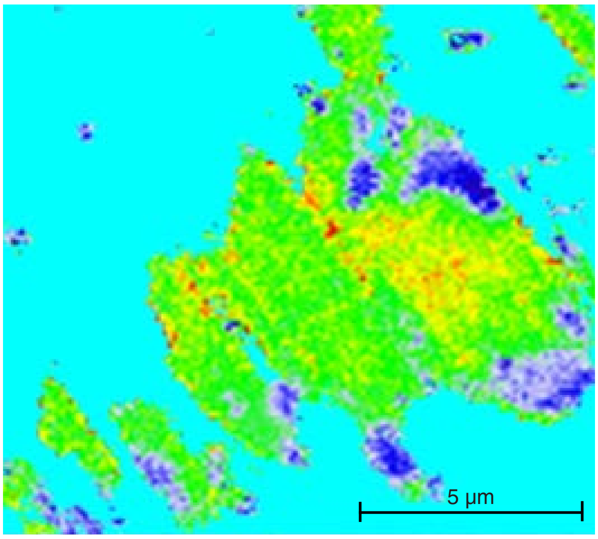
5 Quickly image graphene properties

Quickly image and assess the properties of graphene over large areas, and at high spatial resolutions, using Renishaw's inVia confocal Raman microsocpe and StreamlineHR™ *Rapide*.

Here a Raman map consisting of over 55,000 spectra was collected in under 3 minutes (faster than 300 spectra/s) enabling the number of graphene layers and peak position of the 2D band to be characterised simultaneously.



(a) Raman image of number of graphene layers: bi-layer (yellow); single-layer (orange); areas not containing graphene (cyan)



(b) Raman image of the peak position of the 2D Raman band (an indicator of stress and electronic properties), from the rectangular area in (a)

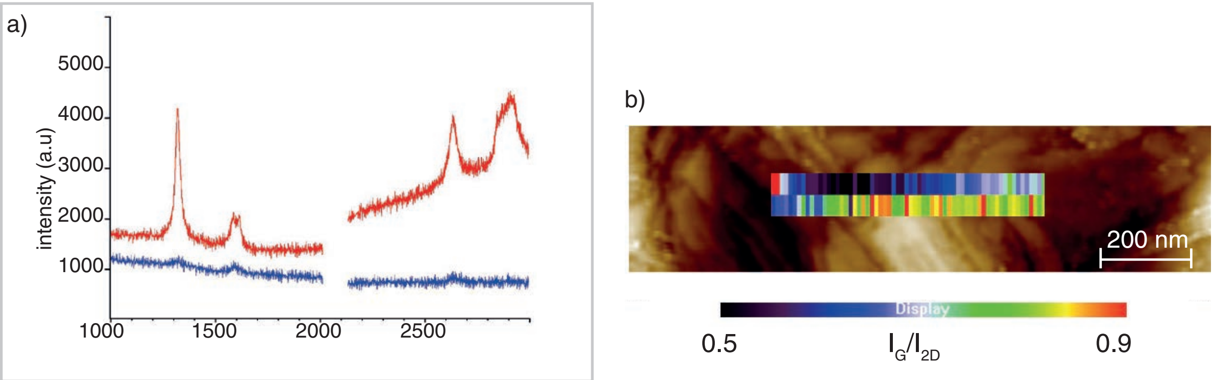
Experimental conditions

Instrument model	inVia confocal Raman microscope
Excitation	532 nm laser
Objective	100× N Plan
Grating	1800 l/mm
Measurement type	StreamLineHR™ *Rapide*
Measurement area	25 µm × 22 µm (0.1 µm step size)
Number of spectra	55,471
Measurement time	170 s

6 Nanoscale imaging using Tip Enhanced Raman Spectroscopy (TERS)

Analyse graphene on the nanoscale by performing Tip Enhanced Raman Spectroscopy (TERS) using inVia combined with an AFM.

TERS uses a special plasmonic tip to increase the local electric field at the sample which, in turn, increases the Raman intensity. The plasmonic tip, referred to as a TERS tip, has an apex size of approximately 10 nm, and is held in close proximity to the sample using an atomic force microscope (AFM) or scanning probe microscope (SPM). The TERS enhancement originates within a few nanometres of the tip and is a near field effect; this allows the spatial resolution of Raman to surpass the diffraction limit. Here TERS measurements were collected from a CVD graphene sample.



a) TERS (red) and regular Raman spectra of graphene (blue), demonstrating the clear enhancement in Raman signal achieved using TERS
b) TERS image superimposed on STM height image. The TERS image highlights significant changes in the intensity ratio of the G and 2D bands, an important parameter used to estimate CVD graphene thickness and quality. Here there are significant changes in the ratio on a 10 nm length scale showing graphene variation on the nanoscale, this variation is not seen using micro Raman which has a diffraction limited lateral resolution of ~ 300 nm. These results can be used to assess the uniformity of the graphene sample on the nanoscale.

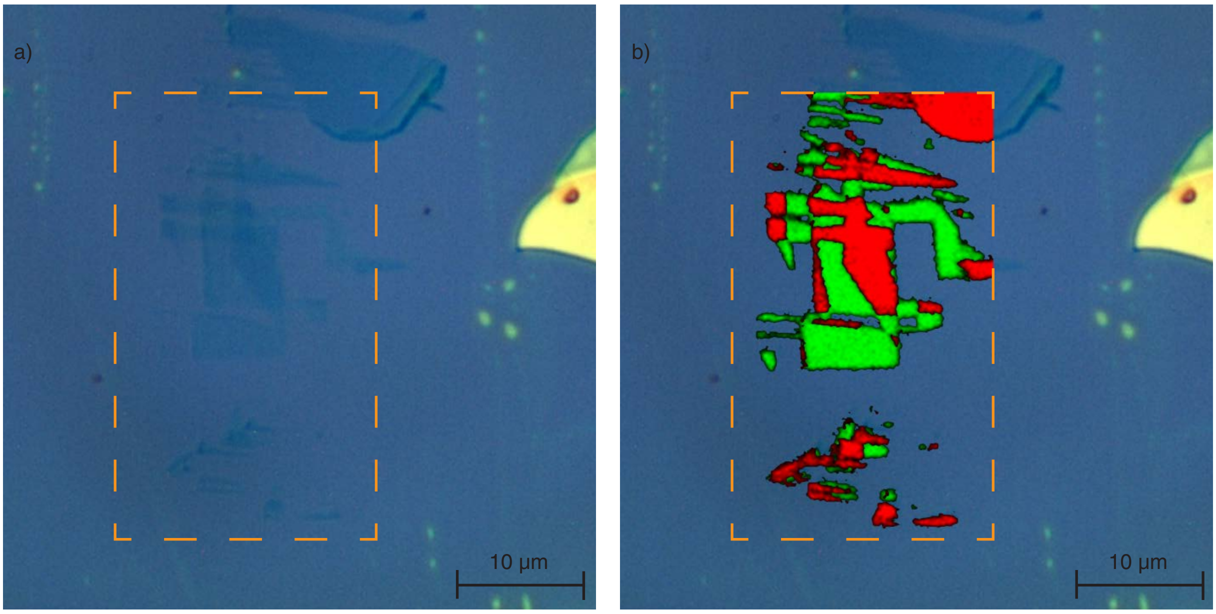
Experimental conditions

Instrument model	inVia confocal Raman microscope coupled to a Bruker Innova SPM
Excitation	633 nm laser
Objective	50× Super long working distance
Grating	1800 l/mm
Measurement type	TERS conducted using Au STM tips
Measurement area	600 nm × 50 nm (10 nm x step, 50 nm y step)
Number of spectra	128
Measurement time	170 s

We would like to thank the University of Cambridge and Thales for providing the CVD graphene sample, for more information on the sample please see Piran R. Kidambi *et al*, J. Phys. Chem. C 2012, 116, 22492–22501

7 Use inVia to locate monolayers of graphene

It is difficult to spot monolayers of graphene in an ordinary optical microscope. With the inVia confocal Raman microscope's StreamLine™ Raman mapping you can rapidly and easily spot graphene and distinguish different layer thicknesses.



A normal microscope image (a) of a silicon wafer coated with discrete graphene flakes. The only clearly visible features are the lighter areas to the right of the image. These contain multiple-layer graphene, which is of little interest to researchers. The highlighted rectangular area appears to be devoid of graphene.
However, a Raman image (b) of the highlighted area reveals that it contains single-layer (green) and bi-layer (red) graphene.
The inVia confocal Raman microscope acquired the StreamLine Raman map data in under 2 minutes.
This example clearly illustrates how you can use inVia to rapidly and easily locate and analyse graphene flakes that would otherwise be undetected.

Experimental conditions

Instrument model	inVia confocal Raman microscope
Excitation	532 nm laser
Objective	100× N Plan
Grating	2400 l/mm
Measurement type	StreamLineHR™ *Rapide*
Measurement area	21.2 µm × 35.4 µm (0.2 µm step size)
Number of spectra	18,762
Measurement time	76.28 s

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8 Further reading

Raman Spectrum of Graphene and Graphene Layers
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Andrea C. Ferrari, and Denis M. Basko
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Raman spectroscopy as a versatile tool for studying the properties of graphene
Andrea C. Ferrari and Denis M. Basko
NATURE NANOTECHNOLOGY, VOL 8, APRIL 2013

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PingHeng Tan, Svetlana Dimovski and Yury Gogotsi
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Adrian T. Murdock, Antal Koos, T. Ben Britton, Lothar Houben, Tim Batten, Tong Zhang, Angus J. Wilkinson, Rafal E. Dunin-Borkowski, Christina E. Lekka, and Nicole Grobert
ACS Nano 2013 7 (2), 1351-1359