

Tip enhanced Raman analysis of graphene

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Abstract

Graphene has huge potential in a wide range of technologies, however for this potential to be realized improvements must be made to enable the growth of higher quality large area graphene sheets. The properties of commercially grown graphene still typically lag behind those of mechanically exfoliated material and new techniques are required to better characterise these materials and optimise growth. In this work we apply tip enhanced Raman spectroscopy (TERS) to a variety of graphene samples, revealing chemical information and often inhomogeneity on the nanoscale.

Raman spectroscopy is a well-established tool for charactering many aspects of graphene, including strain, electronic properties and number of layers [1]. Raman spectroscopy is an optical technique and as such the maximum spatial resolution it can achieve is determined by the diffraction limit, this equates to ~300 nm when using a visible wavelength.

Tip enhanced Raman spectroscopy (TERS) is a novel technique that uses a special plasmonic tip to increase the electric field at the sample which, in turn, increases the Raman signal intensity. These tips are very small, with diameters on the order of 10 nm, and are held in close proximity to the sample using a scanning probe microscope (SPM) or atomic force microscope (AFM). The TERS enhancement originates within a few nanometers of the tip and is a near field effect, allowing the spatial resolution of Raman to surpass the diffraction limit and potentially achieve sub nm resolution [2]. TERS therefore has the unique advantage of increasing both the spatial resolution and sensitivity. Figure 1 illustrates the increase in Raman intensity seen from CVD graphene deposited on Cu. Here preferential enhancement of the D band suggests that a defect region is being directly probed. TERS mapping of the sample reveals variations in G/2D intensity ratio on the 10 nm scale demonstrating the increase in spatial resolution enabled by TERS and also the inhomogeneity of the sample on the nanoscale.

References

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- [2] R. Zhang, Y. Zhang, Z. C. Dong, S. Jiang, C. Zhang, L. G. Chen, L. Zhang, Y. Liao, J. Aizpurua, Y. Luo, J. L. Yang and J. G. Hou, *Nature* 498.7452 (2013): 82-86.
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Figures

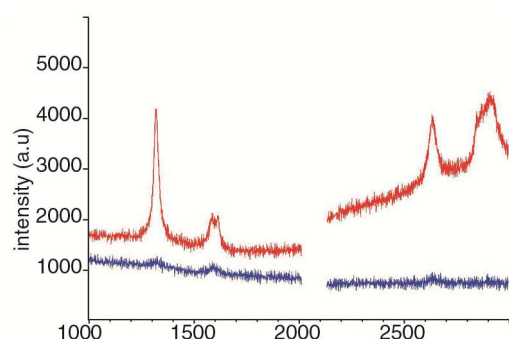


Figure 1. TERS (red) and far field Raman spectra of graphene (blue). These results demonstrate the enhancement in signal provided by TERS. More details on this sample can be found in Ref. 3.

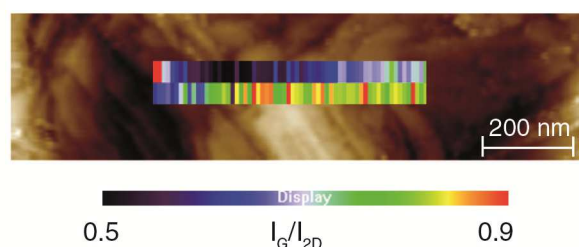


Figure 2. TERS image showing sub-diffraction-limit changes in the G/2D ratio for a graphene sample. This ratio is often used to estimate CVD graphene thickness. Significant changes in this ratio over a 10 nm length scale shows graphene variation on the nanoscale. This variation is not seen using micro Raman which has a diffraction limited lateral resolution of ~ 300 nm.