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Visualizing Carbon Material Properties at Highest Performance and Resolution Using Confocal Raman, AFM, SNOM and SEM

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Introduction

Carbon in its various forms is used in a multitude of macroscopic and microscopic devices. Depending on the device, different material properties are of key relevance to ensure the performance of the devices. Especially for the one and two dimensional form of carbon (i.e. nanotubes and Graphene) the combination of various analytical techniques often leads to the most appropriate understanding of the device.

The aim of this contribution is to illustrate the various fields of application of combined confocal Raman, AFM, SNOM and/or SEM measurements with a focus on carbon materials. The value of nano-carbons for testing state of the art microscopes will also be highlighted.

Materials and methods

New microscopic techniques are developed continuously to improve resolution but also to increase the amount of information obtainable from the samples. The confocal Raman microscope, a combination of a confocal microscope with high sensitivity Raman spectroscopy, provides chemical imaging with diffraction-limited resolution [1]. This technique is capable of characterizing macroscopic tools such as sanding disks or drill heads consisting of diamonds or diamond like carbons in terms of purity, crystallinity, and stress states [2,3]. The same microscopy technique can also be employed to gain information on the distribution of different forms of carbon as filler in various polymeric materials due to the unique Raman bands of the carbon allotropes [4].

For nano-carbon allotropes a combination of the confocal Raman microscope with AFM and SNOM leads to their more comprehensive characterization. AFM provides information about the geometric dimensions of the nano-carbons, whereas SNOM enables optical resolution beyond the diffraction limit while maintaining all optical contrast methods. Furthermore, by combining these two methods with Raman spectroscopy, the resolution of molecular imaging can be improved tremendously.

Results and discussion

The advantage of the combination of Raman and SNOM is demonstrated in Fig. 1. The Raman image presented in Fig. 1a is the integrated intensity of the G band which reveals the presence of a graphene sheet consisting of a monolayer, a double layer and a multilayered graphene (brightest areas). Furthermore, from the intensity distribution of the D band, it is possible to determine the chirality of graphene based on a diffraction limited optical method [5]. Fig. 1b highlights the same sample area, but this time measured in SNOM mode, revealing the transparency of the graphene layers as a function of number of layers (Fig. 1c).

Due to the one- or two-dimensional confinement of nanotubes or graphene respectively, these nano-carbons are ideal materials to demonstrate the resolution and sensitivity of such high resolution, high sensitivity microscopic systems. The one-dimensional carbon nanotubes reveal information regarding the lateral resolution of the confocal microscope (Fig. 2a) whereas the two-dimensional graphene sheets spread on structured silicon substrates reveal the depth resolution and sensitivity of confocal Raman microscopes (Fig. 1b).

Additionally RISE Microscopy is a novel correlative microscopy technique that combines confocal Raman Imaging and Scanning Electron (RISE) Microscopy within one integrated microscope system. A new dimension in imaging: ultra-structural SEM complemented with chemical compound information and molecular Raman imaging (fig. 3).

Conclusions

The large amount of information contained in a Raman image provides information about the molecular and structural composition of carbon macro and nano materials. Combined with high resolution techniques such as AFM, SNOM and/or SEM, these spectral information lead to a more comprehensive understanding of carbon materials can be achieved.

References

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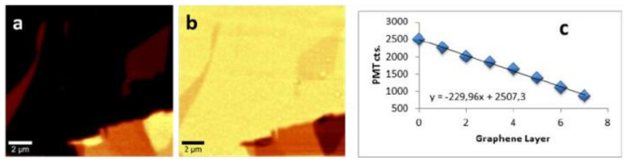

Figure 1. Raman SNOM study of graphene: intensity of Raman G band (a), SNOM image (b), and decrease of transparency of graphene as a function of number of layers.

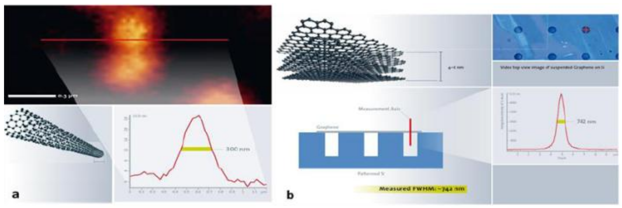

Figure 2. Carbon nano-materials are ideal objects to demonstrate the resolution and sensitivity of high resolution, high sensitivity microscopic systems: lateral resolution of a confocal Raman microscope measured on carbon nano-tubes (a) and depth resolution measured on grapheme sheets spread on microstructures Si substrate (b).

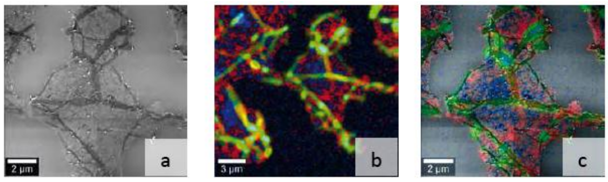

Figure 3. (a) SEM image of a graphene sample. (b) Color-coded confocal Raman image. The colors display the graphene layers and wrinkles. Image parameters: 20 µm x 20 µm, 150 x 150 pixels = 22,500 spectra, integration time: 0.05 s/spectrum. (c) SEM image overlaid with the confocal Raman image.