Measuring the sp^3/sp^2 Carbon Content Ratio in a Single Nanodiamond using Quantitative Optical Microscopy

Nanoparticles have attracted enormous attention in the past decade for applications ranging from photonics devices to labelling and drug delivery in biology and medicine. In the quest for superior photostability and bio-compatibility, nanodiamonds (NDs) are considered one of the best choices due to their unique structural, chemical, mechanical, and optical properties. NDs have shown high biocompatibility in many cell lines and animal models with minimal or no cytotoxicity. They also take advantage of the rich chemistry of organic functional groups such as carboxyls at their surface to enable covalent binding of biomolecules for target-specific labelling [1].

However, the presence of graphitic sp^2 groups at the ND surface is a major limitation for applications, from photonics (unwanted absorption) to mechanics (reduced hardness). These surface groups deteriorate the stability of NDs (graphite is the most stable form of carbon at ambient temperatures and pressures, and the sp^2 groups provide seeds for phase conversion) and can severely affect the particle properties for imaging. For example, it was recently shown by our lab that single non-fluorescing NDs can be visualised using Coherent Antistokes Raman Scattering (CARS) microscopy inside living cells, by exploiting the strong Raman resonance of the sp^3 crystal diamond bond [2]. However, when imaging NDs of radii below about 70nm we noted a rapid degradation of these particles into graphitic carbon. We attributed this effect to the large surface-to-volume ratio of small NDs and consequent absorption from sp^2 surface carbon of the near-infrared pulsed excitation used in our CARS experiment, causing relaxation of diamond into the more energetically stable graphite structure.

To overcome these limitations, several surface modification treatments have been proposed in the literature in order to purify the ND surface. However, reliable measurements of the sp^3/sp^2 carbon content at the single ND level to date require time consuming and expensive electron microscopy approaches. At present, there is no quantitative optical method available to provide this key information.

In this project, we propose to develop, and demonstrate, an optical microscopy tool able to quantify the sp^3/sp^2 carbon content at the single ND level for the first time.

The aim of this project is to develop an optical method to quantitate the size and the sp^2 contamination of single nanodiamonds, and to demonstrate it for NDs in the size ranging from 10 to 200nm.

The method will be based on high resolution optical microscopy, combining **quantitative differential interference contrast** (qDIC) to determine the ND size (i.e. the number of sp^3 bonds), with **photothermal microscopy** to determine the residual optical absorption cross-section by the sp^2 bonds.

In addition, we will apply our recently developed **quantitative widefield optical extinction microscopy** method [3] to single NDs in solution, correlatively with measurements of their zeta potential.

Our goal is to build a multiparameter statistics of the properties of single NDs, correlating the sp^2 contamination with their size and zeta potential. Fluorescence yield of single NDs incorporating defect centres (e.g. NV, SiV) will also be measured (using confocal cryo-fluorescence micro-spectroscopy), and correlated to these ND properties.

[1] V. N. Mochalin et al, Nature Nanotechnology 7, 11 (2012)
[2] I. Pope et al, Nature Nanotechnology 9, 940 (2014)
[3] L. Payne et al, Appl. Phys. Lett. 102, 131107 (2013); Faraday Disc. 184, 305 (2015); Phys. Rev. Applied (submitted)

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