



## Raman spectroscopy study of detonation nanodiamond

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### ABSTRACT

Raman spectroscopy is a technique that is now widely used to study all carbon materials and carbon nanostructures and as such is one of the characterization methods that can be used for the analysis of nanodiamonds. In this paper, we focus on detonation nanodiamonds, the contributions and weaknesses of the method for the understanding of their structure and their surface features are reviewed. The choice of the excitation wavelength, from deep UV to more conventional visible wavelengths, and the choice of the experimental conditions are first examined. In particular, experimental conditions are to be adapted to minimize laser-induced effects and to increase the signal to noise ratio of the spectra. Then, the different features observed for the detonation nanodiamonds, in particular the characteristic diamond peak as well as the one usually assigned as a “G” line, are compared to those that are observed from other origins, HPHT or shock wave. The benefit to use different excitation wavelengths to discriminate between samples is underlined. Finally, the effects of annealing under different atmospheres (in reductive atmospheres, e.g. hydrogen; in an oxidative atmosphere (air, oxygen) and in inert atmospheres: argon or *in vacuum*) were analyzed. Isotopic labelling (deuterated water, <sup>18</sup>O) was also considered. The origin of the “G” line is discussed. In specific cases, high resolution TEM images allowed a better understanding of the observed spectra, showing that size dependent reactivity is another parameter to be taken into account during the analysis of the spectra.

### 1. Introduction

Nanocrystalline or ultra-dispersed diamond, often simply referred to as Nanodiamonds (NDs) belong to a broad family of carbon-based nanomaterials that are promising for a wide range of applications. ND can be available as nanocrystalline thin films using chemical vapor deposition techniques as well as powders via methods such as high-pressure high-temperature synthesis or detonation process. Both kinds of materials have been the focus of several reviews; see for example Refs. [1–5], and references herein. In this paper, particular focus is made on ND powders produced by the detonation process, termed detonation nanodiamond (DND). Details concerning the Raman analysis of nanocrystalline diamond films may be found elsewhere [2].

In the field of material sciences, diamond nanoparticles have great potential for a large variety of applications, including composite materials, lubricants, polishing compositions, electrode materials, seeds for further CVD diamond growth, etc.... In addition, they have recently attracted wide interest in the field of biomedical applications [6, 7] because of their remarkable properties such as low toxicity and

biocompatibility [8–10], possibility of sophisticated surface functionalization [11, 12] and the ability to fluoresce when excited with ultraviolet or visible wavelengths [13]. For all these applications, material purity in terms of sp<sup>2</sup> carbon content as well as a controlled particle size and a well-defined surface termination is mandatory because their surface properties may alter significantly their chemical affinity. Moreover, the surface properties, or more exactly the surface functional groups of DND particles, have a strong influence on the aggregation behavior of the low-concentrated DNDs aqueous suspensions. At present, in spite of intensive works, it has not been clearly understood how the surface of DNDs is arranged.

Vibrational spectroscopies, i.e. infrared and Raman spectroscopies may be considered as methods of choice for the analysis of such DNDs. These two methods are complementary. The fundamental requirement for Raman activity, leading to light scattering, is that there must be a net change in bond polarizability during the vibration for the molecule, the crystal or the functional group under study, while that for infrared spectroscopy is that there must be a net change in dipole moment during the vibration for a transition to be infrared active. These pre-requisites

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mean that these methods may be sensitive to different environments, for example  $sp^2$  bonding using Raman spectroscopy, or polar bonds such as carbon hydrogen or carbon oxygen bonds using infrared spectroscopy.

In that sense, Raman spectroscopy is one of the characterization methods that can be used for the analysis of NDs. More generally, Raman spectroscopy is an experimental technique that is now commonly used to characterize all carbon materials and carbon nanostructures from three to zero dimensions (3D, 0D), such as 3D graphite or diamond, 2D graphene, 1D carbon nanotubes, and 0D fullerenes [14, 15]. Raman spectroscopy has also the ability to distinguish between different forms of amorphous carbon-based materials [16, 17]. Raman spectroscopy of carbons provides not only vibrational and crystallographic information, but also some information about physical properties that are relevant to electrons and phonons. Furthermore, in some specific cases, Raman spectroscopy can also be used to control surface modifications of carbon materials, in particular when strongly conjugated molecules are grafted [18, 19]. In such a case, monolayers can be detected on  $sp^2$  graphitic materials and their chemical or electrochemical reactivity studied.

Initially, the use of Raman spectroscopy was mainly limited to simple identification of the diamond phase through the observation of the so-called “diamond line” at about  $1332\text{ cm}^{-1}$ . However, over the last decade, there is an ongoing effort to understand the different features appearing in the Raman spectrum of DND [20–35] (references listed chronologically). Despite the endeavors thus far, there is still no true consensus on the interpretation of the spectra. This lack of consensus concerns the diamond core of the particle itself as well as the identification of the different surface features. In this paper, we summarize the current understanding of nanodiamond Raman spectroscopy, and also bring new elements of understanding. Here, we limit ourselves to nanocrystals with grain sizes lower than  $\approx 20\text{ nm}$ , for which specific features are expected in their Raman spectra. Such nanocrystals may be provided by the following methods: (i) grinding of HPHT crystals or CVD films, (ii) detonation methods, and (iii) shock wave methods. Here, we discuss the different features observed in their Raman spectra, emphasizing on detonation nanodiamonds.

## 2. Raman measurements on nanodiamonds - issues and solutions

Obtaining Raman spectra of NDs is significantly more difficult than that of CVD diamond films. The first experimental issue is related to the strong photoluminescence (PL) of such materials when illuminated with the usual excitation wavelengths given by visible or near-infrared lasers. Depending on the specimen, the Raman signal is more or less observable superimposed on a huge PL background. In such a case, the Raman signal may be obtained at the expense of intensive baseline corrections. However, such baseline subtractions are often more or less subjective in nature. Because most of the strong PL emission is emitted in the visible and near-infrared frequency ranges, increasing the laser excitation energy to above ca  $3.7\text{ eV}$  effectively allows a clear observation of the characteristic features of the ND Raman spectra. These excitation wavelengths are usually given by He-Cd lasers ( $325\text{ nm}$ ) or frequency-doubled argon ion lasers ( $257$  or  $244\text{ nm}$ ). The benefit of UV Raman spectroscopy to analyze ND was already demonstrated in a number of papers [20, 25, 29].

A second difficulty is related to the inherent low thermal conductivity of fine grained absorbing materials. Actually, the heat conductivity of such powder samples is much lower than that of a crystal or a thin film. Local heating caused by the focused laser light must be taken in account, since it may affect the Raman spectrum even at low laser power levels. Although it may be difficult to quantify the thermal effect, overheating is expected to be all the more important that the grain size is low. In addition, overheating depends on sample packaging as well as the excitation wavelength. To limit the overheating induced by the probing laser beam, the incident power density employed in the

Raman analysis of NDs powder samples has to be at least an order of magnitude lower than that usually used. In particular, it was observed that the use of UV excitations for obtaining PL-free spectra induces considerable sample heating compared to that of the visible ones, and may lead to thermal damage and/or changes in sample composition/structure [29, 36]. Even if no dramatic changes in the shape of the spectra could be observed with respect to the laser power at the samples, some damages at sample surfaces can be visualized using simple optical microscopy. Cooling agents, water in particular, may be used to limit sample heating. However, in most cases, there is a strong overlapping between the Raman spectra of the solvents and the NDs, especially when water is used. Moreover, some possible photo-chemical modifications when using deep UV wavelengths may be anticipated. Thus, a third difficulty should be related to the ND reactivity itself under UV illumination, while most of the measurements are performed under ambient atmosphere. Lastly, a fourth experimental problem is related to the rather low response of such materials, implying long acquisition times when high signal to noise ratios are needed.

Raman measurements presented in this paper were performed using a variety of instruments. The first was a Jobin-Yvon T64000 triple monochromator spectrometer that allowed measurements in both the visible and UV spectral ranges. For this purpose, it was equipped with a UV-enhanced liquid-nitrogen-cooled CCD detector, a microscope, two different confocal optics, and interchangeable gratings ( $2400$ ,  $1800$ ,  $1200$  and  $600$  grooves/mm). The second and third instruments were Renishaw RM 1000 and InVia spectrometers that allowed measurements in the visible, near-UV, and near-IR spectral ranges. They were both equipped with an air-cooled CCD detector and a microscope. For all instruments, a  $50\times$  (numerical aperture or  $NA = 0.85$ ) objective and a UV-dedicated  $40\times$  ( $NA = 0.5$ ) objective were used to focus the laser on the sample surface and collect the scattered light. Similar equipments are used in most published studies dedicated to these “nano-objects”. Recently, the InVia instrument was modified to allow a line excitation at the sample. Line excitation in place of point excitation allows to drastically reduce the irradiance at the sample while keeping high signal to noise ratios. Samples were examined at different excitation wavelengths. The different excitation wavelengths used were the  $785\text{ nm}$  line of a laser diode, the  $514\text{ nm}$  line of a krypton-argon laser, the  $363\text{ nm}$  line of an Argon laser, the  $325\text{ nm}$  line of a He-Cd laser, and the  $244\text{ nm}$  line of a frequency-doubled argon laser. Using the  $785\text{ nm}$  excitation wavelength, spectra were systematically dominated by a strong photoluminescence (PL) background and within some exceptions, it was nearly impossible to extract with certainty the Raman signal of the particles from the PL background. As a consequence, results obtained at this specific wavelength will not be discussed here. Using the  $363$  and  $514\text{ nm}$  excitations, the Raman spectra were also observed superimposed on a strong PL background. This PL background could be fitted to polynomial (cubic) functions or cubic spline interpolations in the  $100\text{--}2500\text{ cm}^{-1}$  wavenumber range and then subtracted to give a Raman spectrum of the nanoparticles. The different procedures used to correct for the PL background led to similar spectra line shapes. Spectra obtained with the  $325$  and  $244\text{ nm}$  excitations were essentially PL-free.

Using point illumination, the incident laser power was first minimized to  $\approx 300\text{ }\mu\text{W}/\mu\text{m}^2$ . However, in such a case, sample heating was still expected [29], and was effectively observed from the downshift and broadening of the diamond first-order mode. Using line illumination, the power density at the sample could be reduced below  $\approx 1\text{ }\mu\text{W}/\mu\text{m}^2$ . Most of the measurement presented here were recorded at  $\approx 10\text{ }\mu\text{W}/\mu\text{m}^2$ , which made it possible to use reasonable acquisition durations, between  $60$  and  $2400\text{ s}$  depending on the desired signal-to-noise ratio.

Purified DND were supplied by NanoCarbon Research Institute Ltd., PlasmaChem (grain size in the  $3\text{--}6\text{ nm}$  range) and Sinta (Minsk, Belorussia, mean size in the  $4\text{--}8\text{ nm}$  range). For comparison purposes, High Pressure High Temperature (HPHT) nanodiamonds (mean

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