



Carbon structure in nanodiamonds elucidated from Raman spectroscopy



Vitaly I. Korepanov^a, Hiro-o Hamaguchi^{a,*}, Eiji Osawa^b, Vladimir Ermolenkov^c, Igor K. Lednev^c, Bastian J.M. Etzold^d, Olga Levinson^e, Boris Zousman^e, Chandra Prakash Epperla^f, Huan-Cheng Chang^f

^a National Chiao-Tung University, Taiwan

^b NanoCarbon Research Ltd., Japan

^c Department of Chemistry, University at Albany, SUNY, USA

^d Technische Universität Darmstadt, Ernst-Berl-Institut für Technische und Makromolekulare Chemie, Alarich-Weiss-Straße 8, 64287, Darmstadt, Germany

^e Ray Techniques Ltd, Jerusalem, 91391, Israel

^f Institute of Atomic and Molecular Sciences, Academia Sinica, Taiwan

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ABSTRACT

Despite their name, nanodiamonds (ND) are comprised of a complex interplay of different carbon phases. The diamond core is surrounded by the shell consisting mostly of disordered sp^3 carbon and graphene-like carbon (GLC). The complex structure makes the characterization of nanodiamonds (ND) a difficult challenge. Recent development of many varieties of NDs for different applications demands quick and reliable characterization of the content of various carbon fragments, as well as the estimation of the diamond core size. In this work, we apply Raman spectroscopy to study the structure of nanodiamonds from different origins, including those produced by detonation (DND), high pressure high temperature synthesis (HPHT), and pulsed laser irradiation (LND). The relative content of GLC, disordered and surface carbon can be easily determined from Raman spectra. In particular, we show how the content of different structure fragments is changed upon de-agglutination, surface oxidation and ion irradiation. We also compare the different ND production methods in terms of the structural uniformity of the nanoparticles. Raman spectroscopy provides unique quantitative tool for ND characterization; we believe that the present data will be useful for understanding the structure of diamond nanoparticles, and will provide the background for obtaining the NDs with desired properties.

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1. Introduction

Diamond nanoparticles represent a unique class of nanoscale systems with variable structure and tunable properties. At present, they can be obtained by several synthetic routes with different grain size ranging from sub-5 nm detonation nanodiamond (DND) to 10–1000 nm high-pressure-high-temperature (HPHT) nanodiamonds. Despite the commonly used term “nanodiamonds”, these nanoparticles comprise a complex interplay of different carbon phases. The structure can be perceived as more or less

crystalline diamond core surrounded by the shell, consisting of graphene-like carbon (GLC), disordered sp^3 carbon and surface-state carbon [1–4]. The latter includes *trans*-polyacetylene (TPA) chains [5,6] GLC islets and fullerene-like fragments [7]. Besides carbon structure fragments, a number of functional groups is found on the surface, including C–H and oxygen-containing groups ($=\text{OH}$, $>\text{C}=\text{O}$), the relative amount of which depends on the chemical history of the sample [8–10]. Some portion of the amorphous sp^3 and GLS shell can be eliminated, for example, by oxidation or plasma etching [11,12]. However, GLC islets, fullerene-like fragments and TPA are intrinsic components of the shell, coming from the re-arrangement of the diamond surface [7]. With the decrease of the particle size, the shell plays increasingly important role in physical and chemical properties of the material.

The wide range of the particle sizes, and easily achievable variety of surface terminations result in numerous applications of

* Corresponding author. Department of Applied Chemistry, Institute of Molecular Science, National Chiao Tung University, 1001 Ta-Hsueh Road, Hsinchu, 30010, Taiwan.

E-mail address: hhama@nctu.edu.tw (H.-o. Hamaguchi).

NDs in biomedicine, material technology, abrasives, lubricants, imaging, and many other fields [2]. The fast and reliable characterization of different carbon phases and their changes upon different physical and chemical treatments is of major importance for the ND-related research and technology. The structure of diamond nanoparticles has been studied previously by many methods, including TEM [1,4], XPS [13–15], and others [10,13–17]. Numerous Raman studies have also been performed, mostly for detonation nanodiamonds. It was shown that Raman spectroscopy is sensitive to the particle size [18,19], can probe the surface functional groups [8] and gives the information on different carbon phases [6,9,20].

In the present work, we attempt a systematic study of the carbon phases content in NDs by Raman spectroscopy. We consider the ND samples of different synthetic origin, commonly used in research and industry, including detonation (DND), high pressure high temperature synthesis (HPHT), and pulsed laser irradiation (LND). We propose a quantification procedure, which allows one to derive the crystallite size information from the Raman pattern, and to analyze how the content of the carbon structural fragments is influenced by the common techniques of ND processing, including de-agglutination, surface oxidation and nitrogen ion irradiation.

1.1. Raman spectra and assignment of the bands

The complexity of ND structure is revealed in the Raman spectra as a superposition of bands coming from the nanocarbon fragments of different bonding [6,20]. The Raman cross-sections for different nanocarbon types also depend on the excitation wavelength in different ways [6]. On the other side, the bands coming from different structure fragments can be easily identified and distinguished, which makes it possible to characterize the relative content of those in the material.

The assignment of the spectral features of different nanocarbons is by now well established; the reader can refer to the works [6,8,20] and references therein for more details. We summarize the spectral assignment in Fig. 1, with the spectra measured at three different excitation wavelengths for the same sample.

The major bands in the Raman spectra of NDs are:

- 1) The diamond band for the bulk crystal is observed as a sharp line at around 1333 cm^{-1} ; for ND it gives a broad peak in $1290\text{--}1350\text{ cm}^{-1}$ region, the position and width depends on the crystallite size.
- 2) Graphene-like carbon gives the G and D peaks, which lie at ~ 1560 and 1360 cm^{-1} respectively [6]. The G peak position shows dispersion (excitation wavelength dependence) [6]. In our experiments, the D peak is most pronounced at 200 nm excitation, while in the 355 and 532 nm spectra it appears as a shoulder. The G band is partially superimposed with the 1640 cm^{-1} band of water [8].
- 3) Disordered sp^3 carbon gives a broad feature in $1100\text{--}1350\text{ cm}^{-1}$, the shape of which corresponds to the density of states (DOS) [20].
- 4) *Trans*-poly-acetylene carbon on the surface gives a peak at around 1150 cm^{-1} [20,21].
- 5) The dumbbell, or split-interstitial defect of the diamond lattice, shows a relatively sharp band at 1630 cm^{-1} [20].

In the present work, we aimed to study the structure of nanodiamonds of different origins, and examine the impact of various treatment procedures on the structure. As can be seen from Fig. 1, most convenient for this purpose is to use the distinct bands of diamond, disordered sp^3 carbon and G-band of GLC measured at 355 nm excitation, because the contribution from non-carbon bands is relatively low, and the bands from different carbon

fragments can be easily distinguished from each other.

It is worth mentioning that there is no general “Raman spectrum of ND”, because the spectral pattern strongly depends on the content of different carbon phases. For instance, the spectrum of the raw detonation soot under 325 nm excitation is dominated by GLC bands to an extent that no diamond peak is observed, and only after oxidation of sp^2 phase the 1327 cm^{-1} peak becomes pronounced [8].

1.2. Experimental detection of the ND Raman spectra

The main difficulty of the experimental detection of ND Raman spectra is that the sample is typically the black powder, which absorbs the light throughout the whole UV–Vis spectral range. Therefore, under the laser beam the sample can be easily heated or burned out. To overcome this problem, different groups either use low laser power or try to measure under water [22]. From our experience, the use of rotating cell with the ND sample dispersed in water allows one to obtain high signal-to-noise ratio spectra without the need to reduce the laser power [23]. In addition to that, this technique helps to avoid the thermal distortion of the phonon spectrum, and provides a good averaging over the sample.

Another challenge is to achieve good signal-to-noise ratio. Most of ND samples give quite strong luminescence, coming, most likely, from GLC fragments on the surface. The luminescence dominates the spectrum at 632.8 nm excitation to an extent that practically no Raman band is observable for most of the samples. With decreasing excitation wavelength the Raman-to-luminescence ratio becomes higher. Under deep UV (200 nm) practically no luminescence is observed. On the other hand, in deep UV spectra many Raman bands from surface groups and defects become quite strong (see Fig. 1) which makes it difficult to analyze the carbon bands. From our results, the reasonable balance is to use UV excitation at 355 nm, under which the luminescence background can be easily subtracted, and the Raman bands of different carbon fragments can be distinguished.

From our observation, the Raman-to-luminescence ratio can also be significantly improved by the oxidation of the surface carbon (e.g. $425\text{ }^\circ\text{C}$ in air), therefore for some measurements the samples can be pre-treated to get better spectra.

1.3. “Raman size” of nanodiamonds

The crystallite size estimation is of major importance for the numerous applications of nanodiamond. The common techniques used for that purpose include transmission electron microscopy (TEM), dynamic light scattering (DLS), X-ray diffraction and small-angle X-ray diffraction (SAXS). It must be understood that these methods by their nature are supposed to estimate different physical parameters. TEM can give the image of the particles at the focal plane, and, therefore, give a rough estimate of the particle size and the crystallite size for a very limited portion of the sample. The DLS measures hydrodynamic radius, which includes surface layers and detects aggregates as a single particle. X-ray diffraction used with the Scherrer equation possesses certain degree of arbitrariness, although for high signal-to-noise ratio diffraction patterns the size distribution of crystallites still can be roughly estimated [24]. The disadvantage of XRD is the low sensitivity to the size. The SAXS is a reliable and sensitive method for estimating the grain size of nanopowders [25]. The grain size although does not coincide with the diamond core size, because SAXS does not make distinction between different types of carbon.

The “Raman size” for crystalline materials can be defined as the phonon confinement length, or, in other words, the size of coherently scattering domain. In case of diamond it corresponds to the

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