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On the structure and impurities of a nominally homologous set of detonation nanodiamonds

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ABSTRACT

Unexpected variations in the purity and structure of commercial detonation nanodiamonds (DNDs) is an ongoing issue. Unfortunately, influences of these variations and how they affect DND behaviors are seldom addressed. This work investigates nominally homologous commercial DNDs sold by a single vendor under the same item number but different lots. Paraffin wax and surfactant were discovered as the major organic contaminants in the DND samples along with metallic impurities. The relative quantities of these contaminants were correlated to discrepancies in the structure and crystallinity of DNDs. The DNDs containing more contaminants possessed thicker shells surrounding the diamond cores; the diamond crystallinity was observed to quickly disappear, on the order of several minutes, when exposed to 200 kV electron beam. On the other hand, those DNDs carrying fewer impurities exhibited a stable diamond structure. The differences in metallic impurities were attributed to variations in the DND purification treatments, and did not appear to affect a morphological change under the electron beam. The present work demonstrates the negative effects of impurities in commercial DNDs on the content and stability of diamond carbons. The results also have implications on possible factors that must be considered when using commercial DNDs for advanced applications.

1. Introduction

Nanodiamonds (NDs) are promising, high-impact carbon (C) nanomaterials for advanced applications in different fields such as coatings, catalysis [1–2], polishing and lubricants [3], adsorbents [4–5], composites [6–7], energy storage [8], and drug delivery systems [9] due to their unique properties [6,10–15]. Although several successful novel chemical syntheses of high purity NDs in microgram quantities have been reported [16–21], the high demand of NDs for research and industrial usage in large quantities still relies on commercial production via detonation of explosives (e.g., [22]). Specifics on the explosives used to produce detonation nanodiamonds (DNDs) are rarely provided. While most reports include reference to the use of cyclotrimethylene trinitramine (RDX) and trinitrotoluene (TNT), it is entirely possible that surplus formulated energetics containing RDX and TNT rather than pure energetic materials, might also be used in the process. If this is the case, the production of contaminated DNDs is a distinct possibility. DNDs are widely recognized as ultrafine particles with diameters of 3–6 nm and structures consisting of diamond cores surrounded by onion-like graphitic layers [14]. Although it is an ongoing issue that the purity and carbon content of DNDs can be easily influenced by a change in one or more procedures during the processes of synthesis, oxidation, stabilization, purification and de-agglomeration [14], different lots of commercial DNDs sold by the same vendor under the same item number are often treated as identical (e.g., having the same manufacturer-provided specifications and properties). As a result, without a thorough analytical characterization of each DND lot, application-dependent conclusions may be erroneously made owing to the oversight of uncertainties in purity and carbon structure in different DND samples.

The relationship between production conditions and the resultant DND properties has been assessed in previous studies. For example, the results of Greiner et al. [22] are one of the first to find the changes in size and shape for both the diamond and graphitic portions in DND grains produced by explosives of different compositions. Huang and Chang [23] also reported similar observations that DNDs with different particle sizes exhibited remarkably different shapes. They found that 100 nm-sized diamonds have rough surfaces and irregular shapes while those with much smaller sizes (such as 5 nm) are mostly rounded. On the other hand, Turner et al. suggested changes in size and shape for DNDs after annealing followed by purification/cleaning with strong acids [24]. Through high resolution transmission electron microscopy

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(HRTEM) images, the diamond cores of untreated DNDs with an average 4.4 nm size already possessed a truncated octahedral morphology for all sizes of annealed DND particles. After the treatment with strong acids, the DNDs became smaller (< 3 nm) and the facets became nearly graphite-free, indicating a complete removal of non-diamond carbons. The dependence of shape and size of DNDs on the synthesis and processing methods was further addressed by Shenderova and McGuire [25]. As produced, the tight aggregates of DND were found to be near-spherical crystals of 5 nm size and consisting of multiple low-index facets in the core with high-index facets on the surface.

The effect of explosive composition was further associated with the detonation temperature and pressure by Kuznetsov et al. [26] who determined that higher RDX concentration in the explosive mixture and higher detonation pressure and temperature led to larger DND particles. The influences of other synthesis conditions were also examined by Baidakova et al. [27] who found that carbon dioxide (CO_2) gas cooling after detonation resulted in DNDs with thicker shells while water cooling led to thinner carbon shells surrounding the diamond cores. The authors also observed phase transformation associated with the (111) planes of the diamond core at an annealing temperature of 1100 K.

Possible variations in the properties of DNDs have been known for a long time and studies on non-carbon entities, their content in DNDs, possible sources, and finding effective methods of removal continue to expand [28–33]. Dolmatov [28–29] proposed that the non-carbon entities react and incorporate into the diamond lattice and are difficult to remove because the surface carbons have no time to stabilize by closing all the bonds in the newly formed diamond lattice underneath during detonation. It is also possible that these non-carbon atoms can be introduced into DNDs by the strong oxidation agents used in purification [28,31,33]. In particular, oxidation of the non-diamond carbon atoms is most likely the main cause for the presence of oxygen atoms in DNDs, which may consist of up to ~10% of the content [28,31]. Once absorbed, these oxygen atoms can attach to both diamond and amorphous carbons as hydroxyl, carbonyl, and carboxyl groups. The hydrogen atoms can chemically bond with diamond carbon atoms [34]. Furthermore, studies have also shown that the hydroxyl and epoxide groups are found to appear locally on some areas but not all surfaces on DNDs. The presence of these non-desirable functional groups have been examined through studying the atomic bonding states of carbon atoms (e.g., [12,23,29,34–35]).

The contents of metal impurities in DNDs are also likely dependent on the quality of water used in purification [28], the materials used for detonator, and the walls of detonation chamber during synthesis [31]. To address the wide discrepancies in purity among commercial DNDs, Mitev et al. [35] identified as many as 55 elemental impurities in 15 commercial DNDs and suggested evaluating the purity of commercial DNDs with 23 elements that are normally at high concentrations. Over the years, several research groups have also explored different methods attempting to remove metallic impurities in DNDs. For example, Dolmatov et al. [30] proposed a new pathway to effectively remove metallic contaminants by using complexing agents and Huang and Chang pretreated the samples with strong acids [23]. These previous studies exemplified the complexity of possible impurities in commercial DNDs and the resultant carbon structure that is introduced during the synthesis and post-processing treatments. Ideally, high-purity diamond carbons should be attained after non-diamond carbons (amorphous and sp^2-C graphene-like onion shells) are either completely removed or transformed after series of processes that involve oxidation, stabilization, washing, and de-agglomeration. However, impurities are still introduced at different stages of production for commercial DNDs, with little information available from the manufacturer to relate the resultant DND structure and composition to the impurities. To better understand the properties of commercial DND samples, this work aims to emphasize the importance of chemical and structural characterizations before any usage of DNDs by investigating the inter-correlation between purity and structure. The techniques employed for this investigation include zeta-potential analysis, desorption, pyrolysis, transmission electron microscopy (TEM), and several spectroscopic methods including laser-induced breakdown spectroscopy (LIBS), Fourier transform infrared (FTIR) spectroscopy, and X-ray photoelectron spectroscopy (XPS).

2. Description of experiments and data analysis

The samples used in this investigation, designated as DND1, DND2 and DND3, were purchased in different batches from Skyspring Nanomaterials Inc. (Houston TX, Product #0510HZ, > 95% C, 3–4 nm), a reseller of DND. Based on the information provided by Skyspring, these samples were produced as three separate lots manufactured by their supplier via nominally identical conditions.

Optical micrographs were obtained using a Carl Zeiss Stemi 200-C microscope and AxioVision software (release 4.8.1).

Desorption and pyrolysis products were analyzed by means of a gas chromatography/mass spectrometry instrument with desorption interface (D/P-GC/MS). Desorption was achieved via a CDS Analytical Model 2000 Pyroprobe (coil type) connected through a heated interface chamber to the splitless injector of an Agilent (Santa Clara, CA) GC–MS system (Model 6890N GC and Model 5973N MSD) with a HP-5 capillary column (0.25 mm × 30 m, 0.25-μm film). The injector temperature was 200 °C; the Pyroprobe interface was set to a temperature of 175 °C. The GC oven temperature program was as follows: 100 °C isothermal for 1 min; 100–250 °C at 40 °C/min; and 250 °C isothermal for 1 min. The Pyroprobe was programmed to give a 20-s desorption pulse at 175 °C at a heating rate of 1000 °C/s. The pulse temperature was based on calibration provided by the vendor and was not measured for this study. Samples (~1 mg) were held within the coil of the Pyroprobe by first placing them in a quartz tube containing a small plug of glass wool, and then inserting the entire tube into the coil. Selected ion chromatograms (SICs) were obtained via Hewlett Packard ChemStation software by extracting specified masses from the total ion chromatogram (TIC).

Laser-induced breakdown spectroscopy (LIBS) was performed on the DND samples using a commercial LIBS system by Ocean Optics, Inc. (LIBS-SC), with a Big Sky CFR200 laser (200 mJ, 1064 nm, 9 ns) and a LIBSCAN2500 7-channel charge-coupled device (CCD) spectrometer (200–805 nm, ~0.1 nm resolution, 1.5 μs delay, 1 ms integration time). Fifteen spectra were averaged for each sample.

FTIR spectra of isolated particles were obtained using a Nicolet is50 FTIR spectrometer interfaced to a Nicolet Continuum infrared microscope operating in reflectance mode and equipped with a Reflacromat 15 × objective. For each spectrum, 128 scans were collected at a resolution of 4 cm^{-1}. Spectral searches were performed using the BioRad KnowItAll® Informatics System (Analytical Edition) software and database.

Zeta potentials and the zeta-average diameters, namely Z-averages, were obtained using a commercial Zetasizer Nano ZSP (Malvern Inc.) by preparing 0.05–0.1 wt% DND suspensions in DI water followed by sonication (Sonicate VWR). The results were the average from three measurements for each suspension. The Z-average was analyzed using the Cumulants technique [36].

Near-surface compositional measurements were conducted using a Physical Electronics VersaProbe II Ultra XPS system equipped with a hemispherical analyzer and a take-off angle of 45°. The sample was irradiated by a focused beam of monochromatic Al Kα X-rays (1486.7 eV). The system pressures are typically around 6.7×10^{-8} Pa when the instrument is idle without argon (Ar) flow, and there is no sample in the main chamber. A survey was acquired of a wide energy range typically 0 to 1100 eV prior to the acquisition of individual elemental high-resolution spectra. The spectra were adjusted for any residual charging by adjusting the energy of the C1s peak corresponding to C—C to a binding energy of 285.0 eV. The chemical compositions were calculated using relative sensitivity factors with the Casa XPS software. The software was also used to deconvolute the C1s