Determination of Size, Morphology, and Nitrogen Impurity Location in Treated Detonation Nanodiamond by Transmission Electron Microscopy

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Size, morphology, and nitrogen impurity location, all of which are all thought to be related to the luminescent properties of detonation nanodiamonds, are determined in several detonation nanodiamond samples using a combination of transmission electron microscopy techniques. Results obtained from annealed and cleaned detonation nanodiamond samples are compared to results from conventionally purified detonation nanodiamond. Detailed electron energy loss spectroscopy combined with model-based quantification provides direct evidence for the sp³ like embedding of nitrogen impurities into the diamond cores of all the studied nanodiamond samples. Simultaneously, the structure and morphology of the cleaned detonation nanodiamond particles are studied using high resolution transmission electron microscopy. The results show that the size and morphology of detonation nanodiamonds can be modified by temperature treatment and that by applying a special cleaning procedure after temperature treatment, nanodiamond particles with clean facets almost free from sp² carbon can be prepared. These clean facets are clear evidence that nanodiamond cores are not necessarily in coexistence with a graphitic shell of non-diamond carbon.

1. Introduction

For over forty years, the scientific community has been fascinated by the properties and possible applications of nanodiamond powder produced by detonation of carbon-based explosives. Many applications like fine polishing, lubricants, CVD growth of larger diamond structures using nanodiamond precursors and hardening of metals and plastics are related to the morphology and physicochemical properties of the diamond nanoparticles.[1,2] Like all diamond-based materials, detonation nanodiamond is a wide band-gap material (Eg ≈ 5.4–5.6 eV), opening the door for unique applications such as UV-blocking and the enhancement of the field emission properties of cathodes in e.g. flat panel displays.[1,2,3]

Recently, detonation nanodiamond (DND) was found to exhibit red photoluminescent properties, allowing detonation nanodiamond particles to be used as optical markers for biological imaging and drug delivery.[4] This photoelectric effect is probably related to defects typical of detonation nanodiamond (mainly twinning) and possibly also to nitrogen-related centers[3] due to nitrogen impurity embedding during synthesis. Much discussion surrounds the exact positioning of the nitrogen impurities within the DND samples: the nitrogen could be sp³ bonded, and therefore deeply embedded within the nanodiamond core, or sp² or sp bonded within the seemingly omnipresent non-diamond carbon shell of the DND particles. Nitrogen could also be a part of the composition of functional groups attached to DND surface (to the diamond core or to the sp² shell) such as amino- or nitro-groups. The corresponding bonding configurations of nitrogen in the functional groups can be sp³ (amino) or sp² (nitro) hybridized. Until now, the nitrogen impurity positioning and concentration has remained unclear. Spatially resolved electron energy loss spectroscopy (EELS) measurements performed on single diamond nanoparticles deposited onto a molybdenum tip point towards an embedding of the nitrogen within the diamond core.[5] The measured particles were however covered to some extent with non-diamond carbon, making definitive conclusions on the positioning of the measured nitrogen difficult. While nitrogen content was only detected in the EELS spectra taken from the central part of a DND particle and not at the edges[5] a possibility that the detected nitrogen was a part of a surface group was not excluded due to the presence of non-diamond carbon. Thus, this issue required additional study.

The main difficulties of the nitrogen impurity measurements in nanodiamond samples are the small scale of the nanodiamond structures, the low nitrogen doping concentration and the
difficulty of producing and measuring DND samples with clean diamond crystal facets (the lack of a graphitic shell would facilitate the nitrogen positioning). In fact, the seemingly ever-present coexistence of diamond and non-diamond phases in DND samples is the cause of a large amount of debate within the scientific community. Many cleaning and etching methods have been developed to remove the graphitic shell from the diamond core, yet non-diamond signals like C–C, C=C, CHx, C=O, and C=O species are frequently measured by several spectroscopic and diffraction techniques on these cleaned samples.[6–13] This led to the development of a diamond core—non-diamond shell model that is now widely accepted.[12,14–16] Within this model, a DND sample can be estimated.

If samples without the presence of a graphitic shell could be produced, the embedding of the nitrogen impurities within the diamond cores would be easier to prove. The faceting of the diamond nanoparticles could also be thoroughly explored for the first time. A first attempt at the imaging of clean diamond nanoparticles was recently undertaken, and lattice resolution images of cleaned nanodiamond were obtained in an aberration-corrected scanning transmission electron microscope (STEM).[17] No clear morphology was observed in these experiments, and lattice resolution was lost after a few seconds of imaging either due to carbon contamination or beam damage caused by the high brightness probe used in aberration-corrected STEM. These experiments clearly showed that all electron microscopy (STEM, but also EELS and high resolution transmission electron microscopy (HRTEM)) of nanoparticles and especially carbon-based diamond nanoparticles is far from trivial. Due to the nature of the diamond nanoparticles any clean particle surface is extremely prone to carbon contamination under the electron beam.[17] All experiments must therefore be undertaken using the minimal electron dose, in order to avoid growing a carbon shell on the clean particle surfaces or inducing damage by a high intensity electron beam.

In the current work, we combine the challenges of accurately and precisely determining the location (embedded within the diamond core, the graphitic shell or being a part of a surface group attached to the diamond core/graphitic shell) and the concentration of nitrogen impurities within detonation nanodiamond samples with the structural and morphological study of annealed, cleaned nanodiamond particles. Model-based EELS quantification methods are adopted to quantify the nitrogen concentration as accurately and precisely as possible.[18–20] Simultaneously, HRTEM investigation allows clear imaging of the DND faceting and determination of the nanoparticle morphology. All microscopy is performed using minimal electron dose, constantly guarding for carbon contamination or beam-induced damage. Three types of DND samples are investigated: a conventionally purified DND reference sample S1, a DND sample with clean facets (with minimal graphitic presence) S2, and samples S3 and S4 with diminished diamond core size (<4 nm) obtained by removing pristine surface groups and some surface layers of the initial diamond particles by high temperature treatment and purification. In the last sample (S4), the presence of nitrogen-containing surface groups on the DND particles is excluded. By comparing the obtained EELS results from all samples, the nitrogen location within DND samples can be estimated.

2. Results

2.1. Luminescence

A typical photoluminescence spectrum of detonation nanodiamond sample 1 measured at 325 nm excitation wavelength presents a structureless broad luminescent band with a maximum at approximately 520 nm (Fig. 1). In recent work, this photoluminescence has been linked to the possible presence of nitrogen—related defects due to nitrogen incorporation and to inherent defects in the nanodiamond particles.[5,21,22] Both the nitrogen incorporation and the defects are studied thoroughly in this work using transmission electron microscopy techniques.

2.2. Electron Microscopy

2.2.1. Size, Structure and Morphology

Detonation nanodiamond particles before and after moderate temperature (300 °C) annealing and subsequent cleaning step are displayed in Figure 2. In Figure 2a, typical DND material prior to annealing is imaged using bright field TEM. The nanoparticles have an average particle size of 4.4 nm, with a narrow size distribution (σ_lognormal = 1.8). The inset ring pattern evidences only the diamond crystal structure (Fd-3m, space group 227) of the particles. No clear ring is present corresponding to the graphite crystal structure, indicating that the shell surrounding the diamond cores is not multi-layered graphite, but single layered graphitic material.[23] After annealing and subsequent cleaning with nitric acid (Sample S2, Fig. 2b) the particles have a smaller average particle size of 3.8 nm (σ_lognormal = 1.5), and their packing is closer. The crystal structure of the particles is not affected by the annealing step, as is evidenced by the electron diffraction ring pattern (inset). Figure 2b is typical for all samples after annealing (S2, S3, and S4). The particles in all the annealed samples are packed closely together, and possess smaller particle
sizes than the original DND specimen. Table 1 lists all the properties of the annealed and the original DND samples.

The effect of the annealing and cleaning steps on the surface of the DND material is made clear by the high resolution images in Figure 3. In Figure 3a, typical DND particles from sample S1 (without any annealing) are imaged. The diamond cores can be clearly discerned and possess a truncated octahedral morphology. A truncated octahedral particle imaged along the [011] zone axis is indicated by an arrow in Figure 3a. The diamond cores are surrounded by a single layered shell of graphitic material, typical for non-treated detonation nanodiamond samples. The effect of the moderate-temperature annealing and subsequent cleaning of sample S2 is made clear by the HRTEM image of a DND particle from sample S2 in Figure 3b. The diamond core is still present, and has an almost unchanged morphology. However, no significant amount of graphite-like material is present on the surface of the diamond octahedron, indicating that the annealing and subsequent cleaning has effectively removed almost all non-diamond carbon from the surface of the particles in this sample.

In Figure 3c, high temperature-annealed sample S3 is imaged. The sample still consists of nanodiamonds, but the particle size is smaller in all high-temperature annealed samples due to the conversion of the diamond surface to graphite, and the subsequent removal of most of the graphitic shell. Sample S3 and S4 both contain a fraction of diamond nanoparticles with sizes smaller than 3 nm, which were not observed in samples S1 and S2. A typical small detonation nanodiamond particle is indicated by an arrow in Figure 3d (sample S4). The particle is

<table>
<thead>
<tr>
<th>Sample</th>
<th>Annealing Temperature</th>
<th>Cleaning method</th>
<th>Particle size [nm]</th>
<th>Morphology</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>–</td>
<td>NaOH/H2O2</td>
<td>4.4</td>
<td>Nanodiamond core – graphite shell</td>
</tr>
<tr>
<td>S2</td>
<td>300 °C</td>
<td>HNO3</td>
<td>3.8</td>
<td>Nanodiamond core</td>
</tr>
<tr>
<td>S3</td>
<td>1100 °C</td>
<td>HNO3, H2SO4</td>
<td>3.6</td>
<td>Small nanodiamond core</td>
</tr>
<tr>
<td>S4</td>
<td>1100 °C</td>
<td>K2Cr2O7, H2SO4</td>
<td>3.2</td>
<td>Small nanodiamond core – graphite shell</td>
</tr>
</tbody>
</table>
approximately 2 nm in size and has a truncated octahedral morphology. The particles in sample S4 (cleaned with H$_2$SO$_4$ and K$_2$Cr$_2$O$_7$) have approximately the same size as the particles in sample S3, but the cleaning with H$_2$SO$_4$ and K$_2$Cr$_2$O$_7$ has not been as effective as that in sample S3 with the HNO$_3$/H$_2$SO$_4$ mixture. More particles possess a graphitic shell in sample S4 than in samples S2 and S3. All size and morphology results are summarized in Table 1.

The small nanodiamond particles formed by the high-temperature annealing are displayed in more detail in Figure 4. Two small particles from sample S4 are displayed together with their Fourier filtered patterns for clarity. The particles are imaged along the [011] zone axis, and are approximately 2 nm in size. Both particles have a truncated octahedral morphology. A model of the particle morphology is displayed below the images in Figure 4, and the same model is also displayed projected along the [011] zone axis. The main surface planes for all the detonation nanodiamond cores are {111}-type, with all imaged surface truncation being {100}-type.

Twinning is the most frequent defect in all the detonation nanodiamond samples,[1,24] and is observed in all the DND samples examined in this study. However, clear differences in the type of twinned structures are observed in the various samples. In Figure 5 three observed twin structure types are displayed. Figure 5c shows a typical 6 nm DND particle showing multiple twinning. Usually, up to three {111}-type twin planes are present in a single DND particle. This type of particle can be found in all the DND samples. Figure 5a shows large multiply twinned structure with an approximate size of 20 nm that is only observed in sample S2. All surfaces and interfaces are almost graphite free, confirming the effectiveness of the annealing step and subsequent cleaning to form graphite-free particles in sample S2. The last twinned structure type is displayed in Figure 5b. It is mostly observed in the high-temperature annealed samples S3 and S4, and shows an elongated structure caused by twinning over large amounts of parallel twin planes.

Figure 4. HRTEM of small nanodiamond particles in sample S4: DND particles displayed together with their Fourier Bragg-mask filtered patterns for clarity. The indicated scale bars are 2 nm. The particles have a truncated octahedral shape (model), with mainly {111} surface planes, and {100}-type truncation.

Figure 5. HRTEM of twinning in the DND samples: (a) Multiply-twinned structure in sample S2. Most of the twinning occurs over a {111}-type twin plane (examples indicated by arrows). The multi twin is imaged in [011] zone axis for most particles. All particles within the multi twin have a truncated octahedral morphology. (b) Elongated twin structure in sample S4, with all twinning over a {111}-type twin plane. (c) Typical DND twinned particle showing three {111}-type twin planes imaged along the [011] zone axis.
2.2.2 Nitrogen Impurity Location

To measure the location and concentration of nitrogen impurities in all the DND samples, detailed EELS measurements were carried out. First, EELS measurements were performed on approximately 100 particles simultaneously in diffraction mode, to obtain the best possible signal to noise ratio and to minimize beam damage or contamination to the nanoparticles. A large spot size with low intensity was used to avoid any possible carbon contamination or damage during the measurements. In Figure 6, core-loss spectra showing the carbon K-edge and tail are displayed together with corresponding low-loss spectra for all four samples. The low-loss EELS spectra in Figure 6b all show a prominent plasmon peak around 34 eV. This is close to the plasmon energy of bulk diamond (33 eV), and far from the plasmon energy for graphite (27 eV) and amorphous carbon (25 eV), confirming that the bulk of the material is diamond.[25] No large amorphous carbon or graphite contribution is measured in any of the samples, indicating a minimal non-diamond carbon presence in all.

In Figure 6a, core-loss EELS spectra for all the samples are displayed. All spectra are aligned to the carbon K-edge onset at 284 eV.[25] The spectra show typical diamond-like ($\sigma^*$) energy-loss near edge structures (ELNES) starting at 292 eV (see diamond reference in Fig. 7). The spectra also show a small carbon pre-peak, typical for graphitic material at 285 eV ($\pi^*$ contribution - see also graphite reference in Fig. 7).[25] A clear signal for nitrogen (nitrogen K-edge) is present in all the samples, with half maximum at 403 eV and peaking at 406 eV. A background subtracted nitrogen K-edge taken from the spectrum of sample S1 is shown in the inset as an example. No oxygen signal (oxygen K-edge at 532 eV) can be detected in any of the samples. This can possibly be attributed to desorption of oxygen-containing groups due to the vacuum and electron irradiation conditions in the electron microscope and requires further study. To determine the nitrogen content in the DND particles, all core-loss spectra were treated using model-based EELS quantification. By using this model-based quantification technique, accurate and most precise nitrogen to carbon quantification results can be obtained.[20] The results are displayed in Table 2. The precision is given by the Cramer-Rao lower bound, the estimated accuracy is taken to be 10%, the common accuracy for Hydrogenic K-edges.[25]

To trace the nitrogen signal within individual particles of the nanodiamond samples and to confirm the findings from the EELS experiments performed on many particles simultaneously, a careful STEM-EELS investigation was carried out on three of the four samples. Sample S1 was measured as a reference material, S2 was measured because of the absence of a graphitic shell in this sample and sample S4, to measure the nitrogen presence in the smaller diamond nanoparticles. In Figure 7, seven STEM-EELS core-loss spectra are displayed. Spectra A through E in the upper panel are taken from the DND samples. The two spectra in the lower panel are diamond and graphite references respectively. Spectrum A is obtained by placing the electron probe on the diamond core of a nanodiamond particle of sample S1. The ELNES of the carbon peak starting at 284 eV is typical for diamond, with a major $\sigma^*$ contribution present. However, a small $\pi^*$ contribution is visible around 285 eV. This small contribution arises from the graphitic shell of the particle that is still measured on the top and bottom of the particle. The nitrogen K-edge is observed with a half maximum at 403 eV (indicated by $\dagger$), indicating the presence of nitrogen at this probe position. Spectrum B is obtained by placing the electron probe on the non-diamond shell of the same diamond nanoparticle from sample 1. The carbon K-edge now shows a larger $\pi^*$ contribution at 285 eV, with a clear pre-peak visible. This peak is indicative of graphitic material and thus confirms the presence of the non-diamond shell surrounding the diamond particle cores. The nitrogen K-edge is not observed in spectrum B. Spectrum C shows the EELS signal taken from a diamond particle from sample 2. All typical diamond features are present, and the nitrogen signal with a half maximum at 403 eV is clearly observed. A small amount of
residual $\pi^*$ contribution remains present. Due to the absence of a substantial graphitic shell in this sample, no shell-position measurement can be given. Spectrum D is obtained by placing the electron probe on the diamond core of a small nanodiamond particle of sample S4. The ELNES is typical, with a major $\sigma^*$ diamond contribution present and a small $\pi^*$ contribution visible around 285 eV arising from the graphitic shell of the particle. The nitrogen K-edge is again observed with a half maximum at 403 eV. Spectrum E is obtained by placing the electron probe on the non-diamond shell of the same diamond nanoparticle from sample S4. The nitrogen K-edge is not observed in spectrum E. Both spectra D and E show more noise than the other spectra, due to the smaller diameter of the diamond particles in sample S4.

Overall approximately 20 percent of all nanodiamond particles that were studied displayed a nitrogen signal in the diamond core. None displayed a signal in the graphitic shell. The nitrogen to carbon ratio was quantified using model-based techniques for the STEM-EELS core-loss spectra. The results of these quantifications are also displayed in Table 2.

### Table 2. EELS model quantified atomic N to C ratios, accuracy and precision for all samples.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Sample</th>
<th>Spectrum</th>
<th>Atomic N to C ratio</th>
<th>Estimated Accuracy</th>
<th>Precision</th>
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<tr>
<td>EELS</td>
<td>S1-bulk Fig. 6 S1</td>
<td>3.1%</td>
<td>0.2%</td>
<td>0.061%</td>
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<td></td>
<td>S2-bulk Fig. 6 S2</td>
<td>3.6%</td>
<td>0.2%</td>
<td>0.072%</td>
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<tr>
<td></td>
<td>S3-bulk Fig. 6 S3</td>
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<td>0.16%</td>
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<td></td>
<td>S4-bulk Fig. 6 S4</td>
<td>3.4%</td>
<td>0.1%</td>
<td>0.13%</td>
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<tr>
<td>STEM-EELS</td>
<td>S1-core Fig. 7A</td>
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<td>S1-shell Fig. 7B</td>
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Figure 7. Background subtracted, normalised carbon K-edge STEM-EELS spectra: Upper panel; (A) spectrum taken from the core of a nanodiamond in sample S1. A nitrogen K-edge is visible with half maximum at 403 eV and peaking at 406 eV (indicated by *). (B) Spectrum taken from the shell of the same particle in sample S1. No nitrogen signal can be discerned. (C) Spectrum taken from a diamond particle in sample S2. A clear nitrogen signal is present. (D) Spectrum taken from the core of a small diamond particle in sample S4. A weak nitrogen signal is present. (E) EELS spectrum taken from the shell of a small diamond particle in sample S4. No nitrogen signal can be discerned. Inset: Z-contrast STEM image showing the measured DND particle from sample S4. The measured probe positions are indicated by arrows. Lower panel; diamond and graphite film spectra taken as reference.

3. Discussion

The main set out of this work was twofold: (i) Localization and accurate determination of the concentration of nitrogen impurities within detonation nanodiamond samples and (ii) the simultaneous determination of the size, (surface) structure and morphology of annealed and cleaned detonation nanodiamond samples. Several annealing and cleaning procedures were used to obtain clean nanodiamond particles (Sample S2) with moderate temperature annealing as well as nanodiamond particles with small particle size (Sample S3 and S4) and clean facets from high-temperature annealing and acid cleaning. Comparing results from these cleaned and annealed samples to conventional DND results would allow localization of the nitrogen impurities. In addition to this information, high resolution imaging of the diamond nanoparticle samples would provide new morphological and structural information on the diamond cores of DND nanoparticles and the change in morphology due to annealing at moderate or high temperature.

The high resolution images presented in Figures 3 and 5 clearly show that the novel moderate-temperature annealing step and subsequent nitric acid cleaning performed on sample S2 successfully removes most non-sp$^3$ carbon from the surface of the
detonation nanodiamond particles. By removing the non-diamond carbon from the sample the truncated octahedral morphology of the particles truly becomes apparent (Fig. 3). The main surface planes of the particles are {111}-type and all truncation imaged is {100}-type. The clean surfaces of the nanodiamonds are however prone to carbon contamination and electron beam damage: high electron doses or prolonged exposure to the electron beam causes formation of a non-diamond carbon shell on the clean facets, just as for the conventional DND samples. This surface transformation under the electron beam is probably the main reason that clean DND facets were not imaged by HRTEM until recently. The moderate-temperature annealing step causes desorption of weakly bonded surface groups and partial buckyfication of the diamond surface layer. This surface layer is mostly removed in the subsequent cleaning step. This leads to smaller diamond nanoparticles in sample S2, with an average particle size of 3.8 nm, compared to 4.4 nm before annealing.

Previously, high-temperature annealing of DND in combination with oxidation using high-temperature treatment in air or graphite etching by hydrogen had been successfully used for deagglomeration of DND aggregates. In our approach we used low-temperature liquid oxidation to remove graphite after high-temperature annealing. This approach allows to preserve smaller DND particles that might still continue to transform to graphite when using a high temperature oxidation or etching procedure. In high-temperature annealed samples S3 and S4 the nanodiamond particles are quite similar to each other. The nanodiamonds are smaller than in conventional samples, with truncated octahedral particles around 2 nm in size being displayed in Figure 4. The fact that the particles retain their truncated octahedral morphology after high temperature annealing means that the graphitization process occurs surface layer by surface layer, and follows the main crystallographic surface planes. From the high temperature treated samples it has become apparent that cleaning with HNO₃ or a mixture of HNO₃ and H₂SO₄ is more effective than using a combination of H₂SO₄ and K₂Cr₂O₇. In HNO₃/H₂SO₄ cleaned sample S3, fewer particles possess a graphitic shell than in sample S4 that was cleaned with H₂SO₄ and K₂Cr₂O₇.

Twinning is known to be a common defect in all DND samples, and can be observed frequently in untreated sample S1. Most twinned particles show up to three twin planes, as the example shown in Figure 5c. Elongated twinning (Fig. 5b) is observed frequently in high temperature treated samples S3 and S4. These elongated structures show up to 6 twin planes in a single structure. Large, multiply twinned structures as in Figure 5a are only observed in clean sample S2. These multiply twinned particles have previously been observed in other detonation nanodiamond samples and are thought to be a result of the synthesis conditions. All interfaces in the multiply twinned particle are non-diamond carbon free, and the surfaces also appear to be clean and sharp.

Knowing that the facets in sample S2 are clean, and that all graphitic material has been removed, makes the EELS data directly interpretable. In Figure 6, all samples show a bulk plasmon in low-loss at the diamond peak position. No major contribution for graphite or amorphous carbon is measured. At this point it is interesting to note that the plasmon measured around 34 eV is the bulk (volume) plasmon for diamond. The authors expected a larger surface plasmon contribution to be detected, as the DND particles have a very small particle size, and therefore a large relative surface to bulk ratio. The presence and size of the surface plasmon is however believed to be subdued due to the close packing of the DND particles (see Fig. 2), a result of sample preparation. This close packing causes the particles to react collectively to incoming fast electrons much as a bulk material.

In the core-loss spectra, a clear nitrogen signal having a half maximum at 403 eV and peaking at 406 eV is present in all samples (see inset Fig. 6–upper panel). This peak position is in good agreement with the σ⁺ contribution of the nitrogen ELNES measured previously in nitrogen-carbon systems. No π⁺ pre-peak is present at 397 eV, a first indication that all nitrogen present in the samples is incorporated into a sp³ coordinated surrounding and thus in the diamond core. Recently, the appearance of the nitrogen peak at 403 eV for nitrogen embedded tetrahedrally into diamond has also been predicted by detailed DFT calculations, confirming our conclusions. The shift in nitrogen peak position to higher energy is not a chemical shift due to N–O bonding, as no oxygen is detectable in the sample. A second indication that the nitrogen is embedded within the diamond cores is given by the quantification of the atomic nitrogen to carbon ratio in the DND samples. Model-based quantification indicated a nitrogen content of around 3 at.-% in all samples. The fact that nitrogen is measured in sample 4 where original surface groups were desorbed and the outer part of DND was converted to graphite shells and stripped using H₂SO₄–K₂Cr₂O₇ indicates that the origin is not nitrogen arising from the cleaning method, but nitrogen originally contained in the DND core during synthesis. The highest atomic N to C ratio is measured in sample S2 (see Table 2). As almost all non-diamond material has been removed in sample S2, it is logical that this material exhibits a higher N to C ratio if the nitrogen is embedded only within the diamond cores. A third and last indication for the incorporation of the nitrogen impurities within the diamond cores is given by the STEM-EELS spectra taken from individual particles in Figure 7. In sample S1, a clear nitrogen signal is measured when the probe is placed on a diamond core, but no signal can be measured when the probe is placed on a periphery carbon shell. This same effect is also measured in sample S4, in a small DND particle. In sample S2, a nitrogen signal is once again detected in the diamond core, and this time with a higher N to C concentration (due to the removal of most of the sp and sp² carbon on the top and bottom of the measured diamond particle). All the EELS measurements therefore indicate that the nitrogen impurities that are deemed to cause the phosphorescent effect in detonation nanodiamond samples are embedded within the diamond nanoparticle core in a tetrahedral coordination (sp³), and are not positioned close to the particle surface or within the graphitic shell.

4. Summary

In the current work, by using a combination of detailed electron energy-loss spectroscopy and model-based EELS quantification on bulk and individual nanodiamond particles, we have...
unambiguously demonstrated that nitrogen impurities deemed to be acting as nitrogen–related color centers in detonation nanodiamond samples are sp$^3$ coordinated nitrogen atoms embedded deep within the diamond core of DND nanoparticles. Simultaneously, we have demonstrated the effect of novel annealing and cleaning procedures on the morphology and twinning of detonation nanodiamond samples, allowing clean, truncated octahedral diamond nanoparticles from moderate-temperature annealing and small DND particles from high-temperature annealing to be imaged for the first time in a conventional TEM. We have shown the need for precise, accurate, and careful characterization of these clean diamond nanoparticles, to guard against contamination of the particle surfaces or electron beam damage that can result in misinterpretation of high resolution TEM images and electron energy-loss spectra.

5. Experimental

Samples: The nanodiamond used in this work was purchased from New Technologies, Chelyabinsk, Russia. The nanodiamond particles were synthesized by the detonation of a mixture of trinitrotoluene (TNT) and hexogen in an ice cooling medium, followed by a soot purification process using a mixture of sulfuric acid with chromic anhydride, washing with water and drying. The average primary size for a detonation nanodiamond was 4 nm based on Rietveld RDX analysis. Additional purification and size fractionation was performed on all samples.

Sample S1 was selected as reference DND material. Sample S2 was cleaned to remove as much of the graphitic shell as possible, while retaining the same diamond core size as the reference sample. Samples 3 and 4 were treated at elevated temperatures and subsequently cleaned, in an attempt to produce nanodiamond material with smaller diamond core sizes, free of non-diamond carbon. In the graphitization/liquid oxidation process applied to samples S3 and S4, all original surface groups on the nanodiamond material were desorbed during annealing and several surface layers of the DND particles were transformed into sp$^2$ carbon and then subsequently removed. Importantly, the liquid oxidizer used for sample S4 did not contain nitrogen, so that formation of new nitrogen containing functional groups on the surface of the diamond cores was excluded.

In detail:

- Sample S1 was purified from metal impurities by boiling in a NaOH/H$_2$O$_2$ mixture followed by washing in deionized (DI) water, treating with ion-exchange resins and drying. Subsequently the powder was dispersed in DMSO and fractionated by centrifugation to the slurry with average aggregate size of 30 nm.
- Sample S2 was annealed at 300 °C, boiled in concentrated HNO$_3$ to remove any graphitic shell surrounding the nanodiamond cores, washed in DI water and fractionated as water-based slurry with average aggregate size of 10 nm. The elemental composition measured using a Carlo Ebra EA1108 CHN Analyzer was C:86.4 wt.-%, H:0.5 wt.-%, N:2.7 wt.-%.
- Sample S3 was obtained by annealing sample S1 in vacuum at 1100 °C and cleaning the resulting material using a mixture of HNO$_3$ and H$_2$SO$_4$ to remove the sp$^2$ shell formed during the annealing step. Following the cleaning step the material was washed with DI water.
- Sample S4 was obtained by annealing sample S1 in vacuum at 1100 °C and cleaning the resulting material using a potassium dichromate (K$_2$Cr$_2$O$_7$) solution in H$_2$SO$_4$ to remove the sp$^2$ shell formed during the annealing step. Following the cleaning step the material was washed with DI water.

DND particles from suspensions of the samples were dispersed on a holey carbon grid for TEM investigation.

Transmission Electron Microscopy and Electron Energy-Loss Spectroscopy: Transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM), and electron diffraction (ED) experiments were performed on a JEOL 4000EX microscope operated at 400 kV with a point resolution of 0.17 nm. Average nanodiamond particle sizes were obtained by measurement of 100 particles, assuming a spherical morphology and using a lognormal particle size distribution.

Electron energy-loss spectroscopy (EELS) and scanning transmission electron microscopy electron energy-loss spectroscopy (STEM-EELS) experiments were performed on a JEOL 3000F TEM/STEM microscope, equipped with a GIF-2000 spectrometer. The EELS experiments were carried out in diffraction mode using a convergence semi-angle $\alpha$ of 0.9 mrad, a collection semi-angle $\beta$ of 1.8 mrad, an energy dispersion of 0.3 eV per pixel and an energy resolution of approximately 1.2 eV. The STEM-EELS spectra were acquired using a convergence semi-angle $\alpha$ of 22 mrad, a collection semi-angle $\beta$ of 29 mrad, nominal spot size of 0.5 nm, energy dispersion of 0.3 eV per pixel and an energy resolution of approximately 1.2 eV. All core-loss spectra were background subtracted, aligned using the onset of the graphitic peak (at 284 eV) and normalized in intensity to their maxima.

To model the core-loss spectra a power-law background AE $^{-r}$ was used. The carbon K-edge and nitrogen K-edge were modeled using a Hydrogenic atomic cross section. Both edges were topped with an equalization function to mimic the density of states. The model was fitted using the Levenberg Marquardt method for Poisson statistics.

Luminescence Measurement: Photoluminescence spectra were recorded at room temperature using a LABRAM HR spectrometer with He–Cd laser for excitation. The laser radiation of $\sim$150 mW power at 325 nm wavelength was focused in a spot of 3 μm in diameter on a surface of a continuous layer (about 1 mm in thickness) of the nanodiamond powder sample.

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[18] The program is freely available under the GNU public license and it can be downloaded from: http://webhost.ua.ac.be/eelsmod/eelsmodel.htm