Aberration-corrected microscopy and spectroscopy analysis of pristine, nitrogen containing detonation nanodiamond

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1 Introduction Nanodiamond synthesized by detonation of carbon-based explosives (detonation nanodiamond or DND) continues to fascinate the scientific community with its versatile properties and plethora of potential applications. Nanodiamond is already used for CVD growth of larger diamond structures, polishing and hardening of metals, and plastics [1]. Many exciting new applications are also being put forward, like graphitized nanodiamond as a battery electrode and supercapacitor material [2–4]. The wide band gap in diamond ($E_g \approx 5.4–5.6$ eV) can also be adopted for unique applications like UV-blocking and the enhancement of the field emission properties of cathodes in e.g., flat panel displays [1, 5].

As a result of its seemingly inherent nitrogen doping, DND is also known to exhibit photoluminescent properties. These properties allow DND particles to be used as optical markers for biological imaging and drug delivery, even in its as-synthesized form (only non-diamond carbon removal steps undertaken) [6, 7], without irradiation to produce vacancies. In native DND, these properties are related to (rare) nitrogen-related centers (NV centers) formed by nitrogen impurities embedded during synthesis as well as to...

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a luminescence originating from amorphous carbon and other defects. Intermittent luminescence from single NV$^-$ centers in as-synthesized 5 nm DNDs was recently measured, paving the road for large-scale production of luminescent particles [8, 9]. Further work showed that the native photoluminescence from NV$^-$ and NV$^0$ centers could be enhanced in DND by a suitable post-synthesis irradiation and illumination procedure [10]. However, a great deal of uncertainty remains about the position and nature of the nitrogen impurities within as-synthesized DND. EPR measurements on native DND species synthesized from a graphite/RDX (cyclotrimethylenetritramine) precursor indicated a concentration of only 1–2 ppm of paramagnetic N (or close to 1 atom in a 30 nm particle) [11] and 0.02 ppm of paramagnetic N in DND produced from a trinitrotoluene (TNT)/RDX mixture [7]. Recent EPR measurements have shown high concentrations of 1 at. % NV centers combined with the same amount of N$_x$ (P1 center) in sintered DND [12], in good agreement with previous spatially resolved electron energy-loss spectroscopy (STEM-EELS) measurements performed by our and other groups indicating more than 2 at. % of N in DND [13, 14]. XPS measurements also demonstrated a far higher concentration of tetrahedrally incorporated nitrogen present in DND [15]. The fact that EPR measurements on native DND were not able to measure high N concentrations leads to the conclusion that most of the nitrogen in native DND must be non-paramagnetic and present in an optically inactive form (such as large nitrogen clusters or enrichment of nitrogen at intrinsic defects in the nanodiamonds [10]) or in a form that is undetectable by EPR (like charge-neutral A-centers). The main difficulties in detecting and distinguishing between the various possible forms of nitrogen in nanodiamonds are the small scale of the nanodiamond structures, the low spectroscopically detectable nitrogen doping and the difficulties of producing and measuring DND samples with clean diamond crystal facets. The latter aspect is particularly important since nitrogen (if measured) could also be present in the graphitic shell.

Being able to produce nanodiamond with a maximal sp$^3$ diamond fraction (and a minimal non-diamond graphitic carbon shell) is a major research challenge [1]. Even though many cleaning and etching methods have been developed to remove the non-diamond shell from nanodiamonds, signals from C–C, C≡C, CH$_n$, C–O, and C=O species are frequently measured by several spectroscopic and diffraction techniques including electron energy-loss spectroscopy on DND [16]. In the past this led to the development of a diamond core – non-diamond shell model that was widely accepted [17]. However, previous experiments carried out by our group showed that diamond particles with a minimal surface graphitic shell could be produced by severe acid treatments [13]. A detailed surface analysis could not be performed, as any clean diamond particle surface is extremely prone to carbon contamination and graphitization at the high acceleration voltages used [18]. These experiments indicated that all transmission electron microscopy and spectroscopy of diamond nanoparticles is far from trivial [16].

In this work we set out to study clean DND, obtained through a recently developed ozone-treatment [19, 20], using a state-of-the-art aberration corrected microscope operated at lowered acceleration voltages (80 and 120 kV). Low voltage microscopy has previously been used to great success in imaging beam sensitive materials like nanotubes, graphene, meteoritic nanodiamond, and hexagonal BN [21–23], and should allow for prolonged experiments to be performed while minimizing the risk of knock-on damage or surface graphitization of the nanodiamond [24]. The surface structure of the clean nanodiamonds is further investigated through the fine structure of the carbon K-edge by high resolution EELS with an electron monochromator.

By combining high resolution imaging with spatially resolved EELS, the nitrogen embedding in single nanodiamonds will be studied. Finally, we will compare the experimental nitrogen K-edge fine structure signature obtained from individual nanodiamonds to calculated spectra obtained from density functional theory (DFT) calculations in an attempt to determine the coordination of the nitrogen impurities in native DND.

2 Experimental

2.1 Sample preparation

The detonation soot that was processed in the ozone treatment reactor was a product of the detonation of a TNT/RDX mixture (40/60 wt.%) with ice as a cooling medium. Prior to the treatment in the ozone purification reactor, the soot was pre-purified of metal contaminants by washing with acids at ambient temperature, followed by a washing in DI water and drying. Subsequently, the nanodiamond sample was ozone purified at 200 °C over 72 h in a fluidized bed reactor, as described in the literature [20].

2.2 (Scanning) transmission electron microscopy and electron energy-loss spectroscopy

High resolution and spatially-resolved EELS experiments were carried out on an FEI Titan 80–300 “cubed” microscope fitted with an aberration-corrector for the imaging lens and the probe forming lens, a monochromator and a GIF quantum energy filter for spectroscopy. High-resolution TEM (HRTEM) experiments were carried out at 80 kV acceleration voltage. The C$_s$ was set to +15 μm for the experiment and the monochromator was excited to provide a 0.3 eV energy spread of the illumination for maximum information transfer. HRTEM image simulations were carried out using the JEMS software package.

The monochromated EELS experiments were performed at 80 kV using a convergence semi-angle $\alpha$ of ~18 mrad, a collection semi-angle $\beta$ of ~108 mrad, a dispersion of 0.03 eV per pixel and at an energy resolution of ~250 meV. The STEM-EELS experiments were performed at 120 kV using a convergence semi-angle $\alpha$ of ~18 mrad, a collection semi-angle $\beta$ of ~60 mrad, an energy dispersion of 0.3 eV per pixel and an energy resolution of approximately 1 eV. The EELS data was fitted with reference spectra for diamond and amorphous carbon to generate the maps in Fig. 4. The
nitrogen map was generated by integration of the intensity under the N K-edge after standard power-law background subtraction in digital micrograph. Prior to N mapping, the EELS data was rebinned by a factor of 4 in the energy-direction to improve the signal to noise ratio of the map. When plotted, the core-loss spectra were background subtracted, aligned using the maximum of the π* peak (at 285 eV) and normalized in intensity to their maxima. EELS quantification was also performed using the digital micrograph software package, using 25 eV wide energy windows for the C–K and N–K edges.

2.3 Energy-loss near-edge structure (ELNES) calculations using density functional theory Ab initio DFT-GGA calculations using the PBE parametrization have been made using the all electron code WIEN2k, based on the full potential linearized augmented plane wave method [25, 26]. The following values for the relevant parameters were used: radius of the muffin tin = 1.35, RK\text{max} (basis cutoff, i.e., the product of the smallest muffin tin radius in the systems and the length of the maximum K-vector of the interstitial plane wave basis) = 6.5; G\text{max} = 14.0. The converged k-mesh for the full Brillouin zone consisted of 2000 k-points for ground state calculations and 750 k-points for the 2 × 2 × 2 supercells used to calculate the ELNES with the core hole. No orientation dependence of the EELS spectra was considered, i.e., the cross-sections were averaged over all possible directions of the scattering vector with respect to the crystal. All structures have been optimized allowing for a change of internal fractional atomic coordinates with default tolerances (convergence on total energy of 2 meV). In some cases an initial elongation of the N–C bond was set by hand and the system was subsequently allowed to relax, according to the procedure adopted by other authors [27]. C and N K-edge ELNES calculations were performed on supercells using the full core hole approximation, i.e., introducing a frozen hole in the excited orbital and smearing the charge uniformly in space. The calculated ELNES spectra were by broadened by 1 eV to accommodate for instrumental broadening.

3 Results
3.1 (High resolution) TEM imaging An overview TEM image of the DND material used for this study is displayed in Fig. 1. The DND particles have primary particle sizes ranging between approximately 2 and 20 nm, and are generally agglomerated into larger structures. The crystal structure of the particles can be determined from the inset electron diffraction pattern; only rings corresponding to the diamond crystal structure (Fd-3m, Space Group No. 227) are present. No graphite or n-diamond [28] reflections are visible, an important indication for a high purity of the DND material. The agglomeration of the DND particles is typical for nanosized materials, and is mainly due to van der Waals attractive forces [29].

A HRTEM image of typical DND particles in the ozone treated sample is presented in Fig. 2a. To acquire this image the electron microscope was operated at 80 kV with the third-order spherical aberration (C3) tuned to +15 μm. To further extend the information limit of the microscope, which is normally limited by chromatic aberration, the monochromator of the microscope was excited to achieve an energy spread of the order of 0.3 eV for the illuminating electron beam. By extending the information transfer of the microscope in this way, intricate details of the nanodiamond surface become visible (see Fig. 2a).

The DND particle is imaged along the [011] zone axis orientation, allowing {111} and {100}-type surface facets and Σ = 3 {111} twin boundaries to be imaged edge-on. Several coherent Σ = 3 {111} twin boundaries run through the imaged particle, as well as a fivefold twin structure (indicated by white arrows). This type of twin is typical for DND as it has the lowest defect energy of all diamond defects [30]. This results from the fact that this twin type only demands a small deviation from the ideal lattice, namely only in the fourth neighbor lattice positions. The abundance of these defects has been attributed to the increased growth rate of twinned nanodiamonds in comparison to untwinned nanodiamond under detonation synthesis conditions [30]. Although the presence of multiple coherent {111} twins was apparent from earlier conventional HRTEM work, several features remained unclear until now. The first is the surface structure, which in this sample exhibits a minimal presence of graphitic carbon. Secondly, the details of the multiple twin boundaries are now clearly imaged; no indication for an enrichment of amorphous carbon or nitrogen clusters at the twin boundaries can be derived from the HRTEM image.

The nanoparticles show mainly {111}-type surface facets with some {100} truncation, a result of the low surface energy of these low-index facets [31]. To illustrate the stability of the nanodiamond surfaces under electron illumination at 80 kV, the same particle is imaged after 3 min.
of continuous electron illumination in Fig. 2b. It is clear that no major changes in surface structure of the diamond particle have occurred over the illumination time, which is in strong contrast to structural changes seen under 200 kV electron illumination [18]. A typical (100) truncation is imaged in more detail in Fig. 2c. Under the imaging conditions used ($C_s = +15 \mu m$, $4 \text{ nm underfocus}$) the atomic columns are imaged in white, as evidenced by the simulation of a truncated diamond particle in Fig. 2c. The combination of the HRTEM image and image simulation allows to conclude that the surfaces (both the $\{111\}$ and $\{100\}$ type surfaces) are extremely clean in the ozone-treated sample. In the region imaged in Fig. 2c, no graphitic surface material can be identified.

To investigate the possibility of detecting substitutional nitrogen atoms or vacancies by HRTEM imaging, extra image simulations were performed (not displayed). It is important to point out that all atomic columns demonstrate similar image contrast in the experimental image. Image simulations using the truncated diamond particle showed no significant change in column contrast when either a vacancy or a substitutional nitrogen atom were inserted into a carbon column. This means that even at extended information transfer, HRTEM cannot be used to locate individual vacancies or substitutional nitrogen atoms and another technique (EELS) will be needed to detect nitrogen in the particles.

3.2 Electron energy-loss spectroscopy
3.2.1 Carbon K-edge ELNES It is well known that the fine structure of EELS edges is related to the local symmetry and environment of the excited atomic species [32, 33]. Therefore, the shape of the carbon K-edge fine structure should provide clues about the form in which carbon is present in the nanodiamond particles. We performed EELS experiments at high energy resolution (monochromator excited to provide an energy resolution of 0.25 eV) to investigate the carbon K-edge fine structure. The carbon K-edge was acquired from several clean nanodiamond particles simultaneously to achieve the best possible signal to noise ratio.

The C–K EELS spectrum in Fig. 3 is dominated by the $1s \rightarrow o^*$ feature starting at 290 eV, which is indicative of carbon in an sp$^3$ coordination. As is typical for DND, a small
Spatially resolved EELS analysis of a multiply-twinned nanodiamond. (a) HRTEM image of a typical DND particle showing the presence of a single coherent twin indicated by A and multiple parallel twin regions indicated by B. (b) ADF-STEM image of the same particle; the white rectangle depicts the STEM-EELS scanned region (53 × 67 pixel spectrum image). (c) sp3 C map, (d) non-sp3 C map, (e) N map, (f) N K-edge spectra from region 1 and 2 indicated in (b). The N content in region 1 is 2.7 ± 0.2 at.%; defected region 2 shows a clear enrichment of nitrogen (3.8 ± 0.2 at.%). (g) Intensity profiles for non-sp3 C (dashed line), sp3 C (black line), and N (bars) taken over the region indicated by the arrow (d) (5 px integration width).

The sp3 carbon map clearly indicates the size of the nanodiamond core, which is almost equal to the particle size from the ADF image. Although only minimal graphitic material was visible in the HRTEM image, the non-sp3 C map clearly follows the surface contours of the nanodiamond particle. The origin of this signal is therefore attributed mainly to some remaining fullerene-like sp2 material and dangling bonds, which can be stable under the UHV conditions in the microscope, at the surface of the nanodiamond particle. A significant non-diamond C signal is also measured from both the coherent Σ = 3 twin boundary (example indicated by A) as well as the lamellar twinned regions (example indicated by B). This signal again arises from sp2 or distorted sp3 coordinated carbon, indicating that even the coherent twin boundaries can deviate from their ideal symmetry, and contain some non-sp3 coordinated carbon [39]. The nitrogen K-edge signal is mapped in Fig. 4e (sp3 C), Fig. 4d (non-sp3 C) and Fig. 4e (N).

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Interestingly, an enrichment of nitrogen at the multiply twinned region is also apparent from the map. The nitrogen
K-edge signal summed over two regions, region 1 being the non-defected diamond region indicated in Fig. 4b and region 2 being the multiply twinned region, are plotted in Fig. 4f. The spectra have been aligned to their continuum level to allow easy comparison. It is clear that both regions contain significant amounts of nitrogen, however, the multiply twinned area is nitrogen enriched as evidenced by the enhanced signal. The nitrogen content in both regions was quantified using standard EELS quantification methods (see Section 2). The average N content in pristine diamond core region 1 is 2.7 at.%. In defected region 2, the nitrogen content is more than 1 at.% higher (3.8 at.%). On the other hand, no clear nitrogen enrichment was measured at coherent twin boundary A (not displayed).

3.2.3 Nitrogen K-edge ELNES As discussed earlier, the EELS edge fine structure is related to the local density of states, and is therefore sensitive to the local symmetry and environment of the excited atomic species. In experiments performed by our own and other groups, the shape and onset position of the nitrogen K-edge led to conclude that nitrogen impurities were tetrahedrally embedded in the nanodiamond particles under study [13, 14].

Untreated and smoothed experimental nitrogen K-edge fine structures from a diamond core region and the experimental carbon K-edge of a nanodiamond particle are plotted in the left panel of Fig. 5. The nitrogen K-edge shows a clear triangular shape, with three defined peaks B, C, and D and a less pronounced pre-peak A, which varies in size depending upon the sample position where the data was acquired. This nitrogen ELNES is similar in other DND samples, even in samples with very high nitrogen doping [14]. Furthermore, the nitrogen and carbon (diamond) K-edge fine structures are clearly similar; peaks B, C, and D are all three present in both spectra. In the case of the carbon K-edge, pre-peak A at 285 eV is related to non-sp³ hybridized carbon [33]. The large degree of similarity between the N and C ELNES indicates that nitrogen is embedded in an environment that is highly similar to that of carbon in diamond, being a tetrahedral setting.

In order to provide more detailed information on the local environment of the nitrogen impurities in diamond, we performed DFT calculations to obtain the nitrogen K-edge ELNES for four different nitrogen centers, being

(i) Single substitutional nitrogen (N, or P1 center)
(ii) Two neighboring embedded nitrogen atoms (A-center)
(iii) The charge neutral nitrogen-vacancy center (NV₀)
(iv) The negatively charged nitrogen-vacancy center (NV⁻)

The DFT calculated spectra, performed in the GGA approximation on 2 × 2 × 2 supercells in the full core hole approximation using the code WIEN2k, are plotted in Fig. 5 [38]. A first impression is that all four calculated N–K edge spectra look similar. This is a result of the similar coordination of nitrogen coordination in all four cases. Even though the spectra look similar, small differences can be made out between them. The spectra for both NV centers are quasi-identical, and are visually different from the experimental nitrogen K-edge. Even though all the calculated spectra have been broadened by 1 eV to take into account instrumental broadening in the experimental data, the spectra for NV⁻ and NV₀ are narrower and less defined than the experimental spectra. This is a confirmation of other data present in the literature that shows that the nitrogen present in as-synthesized nanodiamond is not present in the form of NV⁻ or NV₀ centers in sizeable amounts [10]. Significant numbers of these defects can only be generated in DND after application of proper vacancy creation and sintering treatments [1, 12, 40].

The spectrum for single substitutional nitrogen N is more triangular in shape, similar to the experimental nitrogen K-edge ELNES, reproducing features B, C, and D as well as a pre-peak to the main feature B. This pre-peak is a \( \pi^* \) contribution that arises from bond length elongation of one of the C–N bonds by approximately 30%, a result of the energy relaxation step in the calculation, which is in good agreement with the literature [27]. Owing to this elongation, the coordination of the substitutional nitrogen atom is more planar with respect to the other 3 bonding carbon atoms, giving rise to the \( \pi^* \) contribution [41]. As was the case for the calculated NV center spectra, the \( \text{N}_0 \) spectrum is less broad than the experimental nitrogen K-edge.

The calculated spectrum for the A-center model (2 neighboring, substitutional nitrogen atoms) provides the best
match with the experiment. Peaks at B, C, and D are reproduced correctly, with peak positions that fit well with the experimental ones. Pre-peak A, which is present in the experimental ELNES, is however not reproduced by the A-center model. This result differs from earlier ELNES simulation work using multiple-scattering theory, in which pre-peak A was reproduced [41].

4 Discussion This work concentrates on the morphology and surface structure of pristine DND and the distribution and nature of nitrogen in as-synthesized nanodiamond powder. Powders that were previously treated in an ozone process show clean surfaces with a minimal graphitic (non-sp\(^3\)) surface shell.

Many nanodiamond particles show the presence of coherent twin defects in HRTEM images due to the fast out-of-equilibrium synthesis conditions [30]. The improved resolution offered by aberration-corrected microscopy, in combination with imaging at lower acceleration voltages below the C knock-on damage threshold allows the particles to be imaged over prolonged periods, without graphitization of the nanodiamond surface, as evidenced by the data in Fig. 2a, b. Owing to this added surface stability, any detected non-sp\(^3\) material arises from the material itself and is not an imaging artifact. HRTEM imaging confirms the presence of mainly \{111\}-type surface facets in the DND material, with some \{100\} type truncation present. No significant amounts of \{110\} surface planes are present, confirming that the high-energy, fast detonation synthesis favors formation of rapid growth \{111\} and to a lesser extent \{100\} surfaces, as well as low-energy defects like \(\Sigma = 3\) \{111\} twin boundaries [30].

Even though HRTEM imaging can be used to visualize the surface structure of the nanodiamond particles, the presence of nitrogen or a small amount of non-sp\(^3\) coordinated carbon at e.g., coherent boundaries cannot easily be imaged. The presence of non-sp\(^3\) coordinated carbon was confirmed through three distinct C K-edge pre-peak EELS signatures in Fig. 3. Image simulations with single nitrogen atoms substituting for carbon yielded no discernable image contrast changes, meaning that detecting single nitrogen atoms substituting for carbon yielded no peak EELS signatures in Fig. 3. Image simulations with carbon was con...
5 Conclusions Aberration-corrected electron microscopy allowed us to solve several remaining key questions about the (surface) structure, morphology and the presence of nitrogen impurities in DND. We were able to image clean, stable nanodiamond facets at true atomic resolution for the first time – evidencing that clean nanodiamond facets are feasible, and that the core–shell model for nanodiamond is not necessarily representative for materials that have undergone sufficiently harsh surface cleaning treatments. Core-loss EELS spectrum imaging experiments prove the presence of nitrogen in DND particles, spread out within the “core” of the particles and in some cases enriched at defective regions as well as at twin boundaries, with a maximal nitrogen content around 4 at.%. DFT calculations of the $N_s$, $A$, NV$^0$, and NV$^-$/center N–K edge ELNES signatures were performed. By comparing the fine structure of the experimental nitrogen K-edge with the calculated spectra, the embedded nitrogen is shown to likely be a mix of some small amounts of single substitutional and/or A-center nitrogen, combined with larger nitrogen clusters.

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