Nitrogen Control in Nanodiamond Produced by Detonation Shock-Wave-Assisted Synthesis

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Supporting Information

ABSTRACT: Development of efficient production methods of nanodiamond (ND) particles containing substitutional nitrogen and nitrogen-vacancy (NV) complexes remains an important goal in the nanodiamond community. ND synthesized from explosives is generally not among the preferred candidates for imaging applications owing to lack of optically active particles containing NV centers. In this paper, we have systematically studied representative classes of NDs produced by detonation shock wave conversion of different carbon precursor materials, namely, graphite and a graphite/hexogen mixture into ND, as well as ND produced from different combinations of explosives using different cooling methods (wet or dry cooling). We demonstrate that (i) the N content in nanodiamond particles can be controlled through a correct selection of the carbon precursor material (addition of graphite, explosives composition); (ii) particles larger than approximately 20 nm may contain in situ produced optically active NV centers, and (iii) in ND produced from explosives, NV centers are detected only in ND produced by wet synthesis. ND synthesized from a mixture of graphite/explosive contains the largest amount of NV centers formed during synthesis and thus deserves special attention.

INTRODUCTION

A central focus of many research groups is a controlled production of the nitrogen-vacancy (NV) centers in nanoscale diamond.1–9 Due to strong optical transitions, single defects can be detected using the fluorescence microscopy technique. The spin state of the negatively charged NV centers can be polarized by optical pumping and can be manipulated using the electron paramagnetic resonance (EPR) technique, permitting the implementation of efficient single photon emitters for quantum information processing10–13 or a magnetic sensor with nanoscale resolution.14,15 Single color centers show outstandingly high photostability, even at room temperature.1,16,17 Thus, on-demand production of NV centers in nanodiamond (ND) is important for several emerging applications like quantum information, nanoscale sensing and photoluminescent markers for microscopy (including superresolution techniques).18

The development of bright photoluminescent NDs has mostly focused on diamonds produced by high-pressure high-temperature (HPHT) synthesis under static conditions (containing 10–300 ppm of native substitutional nitrogen defects (N_i)), ground to nanosized particles.1–3,16,17 To produce the NV centers, either the initial diamond material or nanoscale diamond particles produced by grinding are irradiated with energetic particles (e.g., electrons, protons, etc.) to create vacancies. Subsequent annealing in vacuum at 600–800 °C causes vacancy diffusion and formation of the NV centers. With another approach nanodiamond crystals containing single color centers have been grown by chemical vapor deposition (CVD).1 Formation of the NV centers by carefully controlled implantation of N ions into high-purity CVD diamond films followed by annealing is also under development.5,19

A large subgroup of nanodiamond is produced via so-called dynamic synthesis, harnessing the energy of explosives and different carbon-containing precursor materials.20 Three classes of NDs synthesized by shock-wave-assisted methods are manufactured on an industrial scale: (i) NDs produced by direct phase transformation of graphite induced by an external detonation shock wave (the DuPont method); (ii) NDs produced from the carbon
contained in high-energy explosives themselves (so-called detonation ND (DND), or ultradispersed diamond\(^ {23} \)); (iii) NDs produced from a mixture of a carbon precursor and explosives.\(^ {23} \)

Depending on the precursor material in the shock-wave-assisted synthesis, NDs with single crystal particle sizes between 4 and 25 nm can be synthesized.\(^ {20} \) Slurries of 4 nm individual DND particles\(^ {22} \) or NDs synthesized from graphite and graphite/hexogen precursors with average aggregate size of 20–30 nm are commercially available. Optical/photoluminescent properties of NDs produced from a graphite and graphite/hexogen mixture were not studied before, while several attempts to produce photoluminescent DNDs synthesized from a mixture of explosives (TNT/hexogen) have already been undertaken.\(^ {6–9,25} \) Due to previous unsuccessful attempts to significantly increase photoluminescence in irradiated and annealed DND\(^ {28} \) and because of negative conclusions on the energetic stability of N in 2 nm NDs based upon atomistic modeling,\(^ {28} \) the prognoses of producing the NV centers in DND were highly pessimistic until recently. All earlier attempts to detect paramagnetic nitrogen in detonation nanodiamond using the traditional continuous-wave (CW) EPR technique were also unsuccessful.\(^ {27} \) Strong, broad EPR signals presumed to originate from surface defects of DND particles dominated the EPR spectra, preventing observation of any other paramagnetic defects typical for bulk diamond.

However, within the last couple years several new characterization methods have been applied to detonation ND, evidencing the presence of substitutional nitrogen and NV centers in irradiated and even in as-synthesized DND. First, the presence of NV centers in proton irradiated DND produced from TNT/hexogen mixture was revealed using time-resolved luminescence spectroscopy.\(^ {8} \) Later, studies were performed on individual DND particles, doing so dramatically decreasing the PL background from bulk material related to ND surface structural defects. As a result Vlasov et al.\(^ {8} \) could observe stable photoluminescence from NV centers in large electron-irradiated DND particles (sizes >20–30 nm) using conventional PL spectroscopy. Later, Bradac et al. detected NV centers in individual nonirradiated 5 nm DND particles produced from TNT/hexogen by a wet synthesis method.\(^ {7} \) Unexpectedly, intermittency in the luminescence depending on the local environment of the single DND particles was observed.

Analysis of the substitutional nitrogen atoms in ND produced from a mixture of explosives (TNT/hexogen) has also progressed significantly. Smith et al.\(^ {8} \) estimated the N concentration in DND by pulsed EPR to be similar to HPHT diamond crystals and Turner et al.\(^ {28} \) presented evidence for tetrahedral N coordination in DND from electron energy-loss spectroscopy. Fionov et al.\(^ {29} \) estimated the concentration of paramagnetic nitrogen in DND to be 2 ± 1 ppm, by modeling and subtracting the broad background in CW EPR spectra. EPR signals from paramagnetic N\(_ {e} \) have also been detected using pulsed EPR in DND sintered under HPHT treatment\(^ {9,30,31} \) (800 °C and a pressure of 6 GPa) and in as-produced DND powder.\(^ {31} \) When the sintering temperature is 800 °C (vacancies start to diffuse), the presence of a significant amount of NV centers (up to 1% or 10,000 ppm) is detected in 10 \( \mu \)m aggregates using pulsed EPR.\(^ {31} \) Recently, nitrogen paramagnetic centers in concentrations of 1.2 ± 0.5 ppm were detected by pulsed EPR in ND produced from a graphite/hexogen mixture.\(^ {22} \)

These findings indicate that NDs synthesized by detonation shock-wave-assisted methods deserve a more thorough investigation of the nitrogen content, N location in the ND core and its ability to form optically active centers through the creation of complexes with vacancies. It will be demonstrated below that depending on the synthesis method and precursor material, the average ND crystal size and N content can be varied. ND produced by detonation of explosives in a highly nonequilibrium process contains various defects including vacancies and vacancy complexes.\(^ {30} \) Since the precursor material (explosives) contains nitrogen and a proper choice of the soot cooling conditions can presumably control the vacancy kinetics, in situ formation of NV centers during synthesis might be possible. In situ production of NV centers in ND of dynamic synthesis has the advantage of being industrially viable while avoiding costly irradiation and high-temperature annealing treatments currently applied to HPHT ND.

In this paper, we have systematically studied several types of dynamically synthesized NDs produced from different carbon precursor materials, namely, from graphite and a graphite/hexogen mixture, as well as DND produced by several combinations of explosives and cooling methods. ND crystal size, morphology, N content, and N state (single substitutional atoms or complexes with vacancies) were characterized using X-ray diffraction and scattering, high-resolution transmission electron microscopy (HRTEM), electron energy-loss spectroscopy (EELS), Raman spectroscopy, pulsed EPR, and a combination of atomoc force microscopy (AFM)/confocal photoluminescence spectroscopy.

### RESULTS

Five samples representing NDs produced from different carbon precursor materials via detonation shock-wave-assisted methods have been investigated. The carbon precursors were graphite (sample ND-G) and a graphite/hexogen mixture (ND-G/RDX). In addition, DND produced by various combinations of explosives (ND-TNT/RDX and ND-TNT/HNS) and cooling methods (ND-TNT/RDXw and ND-TNT/RDXd, denoting wet and dry cooling methods, accordingly) were studied. Table 1 and Figure 1 summarize sample notations and the synthesis details.

#### Morphology and Microstructure

The phase composition and size distribution of the nanodiamond crystallites in the ND powders are analyzed by X-ray diffraction (XRD) and small-angle X-ray scattering (SAXS). The XRD patterns are shown in Figure 2. For all samples the diamond phase dominates. However, the presence of various (minor) amounts of graphitic carbon is also observed (peak at ~26.9°). The diamond 111 diffraction peak is often nonsymmetric. The observed shoulder is due to an overlap of the diamond 111 and graphite 101 peaks. In addition, several diffraction peaks (100, 002) of hexagonal diamond (h-dia)—lonsdaleite—may also contribute to the main peak.

The overlap of the peaks from diamond and graphite (hexagonal and rhombohedral) polytypes makes a reliable determination of the crystal size of the corresponding phases difficult. Panels A and B of Figure 2 show examples of decomposition of the main peak into

| Table 1. Sample Notations and Details of the Synthesis |
| --- | --- | --- |
| sample | carbon precursor | synthesis conditions (cooling) |
| ND-G | graphite | mixture of graphite and metal powder |
| ND-G/RDX | graphite/RDX (20:80) | dry (nonoxidizing gas) |
| ND-TNT/RDXw | TNT/RDX (40:60) | wet (ice) |
| ND-TNT/HNSw | TNT/HNS | wet (ice) |
| ND-TNT/RDXd | TNT/RDX | dry (nonoxidizing gas) |
several components (Pearson VII shape of the peaks is assumed). The dimensions of the diamond crystallites are estimated from the Debye–Scherrer formula and are approximately 13.6 nm for the 111 reflection and 9.6 nm for the 110 peak for the ND-G/RDX150 sample; 8 nm for the ND-G sample and 4 nm for DNDs produced from explosives. A very rough estimation of the possible lonsdaleite grain size gives ∼2.4 nm for the ND-G sample. This value is similar to the one reported by Trueb and Kurdyumov et al. for h-dia produced by shock-conversion of graphite and is considerably smaller than the sizes of the cubic diamond crystallites.

The size distribution of the scatterers was obtained from SAXS data by assuming a spherical morphology and is shown in Figure 3. For all samples the crystal size of the dominant fraction determined by SAXS is larger than the size determined from the broadening of the Bragg peaks. This can be explained by the different principles used for size determination in both techniques (Figure 3D). The width of the Bragg peaks in a XRD pattern reflects the size of so-called “coherently scattering domains” which is usually smaller (rarely equal) than the entire particle size. SAXS is based on the electron density contrast between the scatterer and the surrounding medium, thus providing information about the overall size of a nanodiamond particle. The discrepancy in the crystal size determined by both techniques reflects the fact that diamond particles consist of several crystallites within a single grain.

The SAXS data for the ND-G sample (Figure 3A) show a bimodal size distribution of the particles with peaks (diameters) at ∼6 nm and at ∼23 nm. Unfortunately, the SAXS curves do not allow one to unambiguously determine whether the “small” and “large” particles represent different phases or not. The size distribution for the ND-G/RDX sample (Figure 3B) differs considerably from the majority of the nanodiamonds studied within this work, since this sample possesses a relatively broad size distribution centered at ∼34 nm. Finally, the size distribution of the nanodiamonds produced from explosives (Figure 3C) is typical for detonation nanodiamonds: the main peak shows diameters around 6 nm and a broad tail stretching out to larger sizes. It should be noted that the fraction of particle crystal sizes exceeding 6 nm is larger for ND of dry synthesis as compared to ND of wet synthesis (Figure 3C). The secondary peaks at larger sizes in DND of dry synthesis most probably belong to a graphite phase, since nanodiamond particles with grain sizes larger than 10 nm were not observed by HRTEM for this sample.

Table 2 summarizes the size measurements of the primary crystallites (XRD data), ND particles (or grains) (SAXS data), and the average aggregate size of the studied samples dispersed by sonication in deionized water.

The nanodiamond morphology and grain size were further verified using transmission electron microscopy. Figure 4 shows (HR)TEM images of samples ND-G/RDX150 (a), ND-G (b), ND-G/RDX40 (c) and ND-TNT/HNSw (d). Samples ND-G and ND-G/RDX40 are highly similar, showing abundant large, rounded or elongated diamond particles without a clear morphology or showing only high-index facets. These structures often consist of agglomerates of smaller particles (see (b) and (c)) and show the presence of large amounts of defects in the diamond lattice. These particles can also be found in sample ND-G/RDX150, but in...
combination with rounded or well-faceted polyhedral and truncated octahedral particles with low-index facets. The smaller particles below 6 nm in diameter show mainly \{111\} and \{100\} facets typical for small DND particles, while larger particles also show higher index facets (see (a)). These particles show the presence of coherent \(\Sigma = 3\) \{111\} twinning, common for detonation nanodiamond (examples of twinning are indicated by arrows in (a) and (d)). The absence of well-faceted polyhedral particles in the sample ND-G/RDX40 demonstrates that these particles were removed during centrifugation of the sample ND-G/RDX150.

Samples ND-TNT/RDXw, ND-TNT/HNSw, and ND-TNT/RDXd are typical DND samples with small particles in the 4–6 nm size range, showing low index \{111\} and \{100\} facets covered to a large extent by amorphous surface carbon or graphite. Similar to sample ND-G/RDX150, these small nanoparticles show abundant coherent \(\Sigma = 3\) {111} twinning, a result of the rapid particle growth mechanism in DND synthesis or of mechanical twinning induced by the reflected shock waves.\(^{38}\) We have previously shown that large, multiply twinned particles with diameters up to 100 nm can occasionally be found in sample ND-TNT/RDXw.\(^{6}\) A summary of the morphology of the samples is given in Table 1S of the Supporting Information and the sizes are summarized in Table 2.

Raman spectra of the samples were acquired in a range of 1200–1700 cm\(^{-1}\) (Figure 5). Typically the first-order Raman spectrum of highly purified DND consists of two peaks. The first one is located in the vicinity of 1332.5 cm\(^{-1}\) and corresponds to the vibrational mode of a diamond lattice from the center of its Brillouin zone. The origin of the second one observed at 1630 cm\(^{-1}\) is still a subject of debate.\(^{39-41}\) Four of the samples demonstrate these two peaks in their spectra (spectra 1–4, ND-TNT/RDXw, ND-TNT/RDXd, ND-TNT/HNSw, and ND-G/RDX40 samples). When an
The abundance of sp²-bonded carbon clusters is present in DND, another two peaks characteristic of sp² carbon appear between 1350 and 1380 cm⁻¹ (the D-band) and 1580–1610 cm⁻¹ (the G-band). These peaks are observed on spectra 3 and 4 (ND-TNT/HNSw and ND-G/RDX40 samples). The abundance of sp²-bonded carbon can be so high that the diamond and 1630 cm⁻¹ peaks become indistinguishable from the background of D and G bands, as is observed for the sample ND-G (spectrum 5). Note that the Raman spectrum of the initial sample ND-TNT/RDXd is similar to spectrum 5 in Figure 5 (ND-G sample), indicating that a high content of sp²-bonded carbon is present in this sample. Extraction of the 6 nm primary particles from the sample and additional purification allowed us to efficiently remove the graphite-like carbon and to obtain a Raman spectrum (2 in Figure 5) which is similar to the spectrum (1 in Figure 5) of the highly purified ND-TNT/RDXw sample. All three samples of detonation-type synthesis demonstrate a shift in the diamond Raman line down to 1328.5 cm⁻¹ (see Table 2) which is explained by the phonon confinement effect observed for small nanocrystals.42 Earlier we reported on the 1326 cm⁻¹ position for the Raman line of the sample ND-TNT/RDXw.6 The Raman spectrum in that work was measured for a dry powder. In this case it is difficult to exclude overheating, a possible reason for the larger shift in the diamond peak position. Despite highly variable nitrogen concentrations in these three samples of detonation synthesis (see below), the shifts are constant. This means that a high concentration of nitrogen (up to 2–3% mass) in some samples does not influence the Raman phonon of the nanodiamond lattice. This could be explained by assuming that nitrogen mostly forms agglomerates in diamond lattice instead of being uniformly distributed in substitutional or interstitial form. Large primary particles of the sample ND-G/RDX40 are not

Table 2. Size of Coherently Scattering Domains Determined from XRD and Crystal Sizes Obtained from SAXS and HRTEM and Position of the Diamond Raman Peak for Different Classes of Nd of Dynamic Synthesis

<table>
<thead>
<tr>
<th>sample</th>
<th>size from XRD, nm</th>
<th>size from SAXS, nm</th>
<th>size from HRTEM, nm</th>
<th>average size of agglomerates, nm</th>
<th>Raman diamond peak position, cm⁻¹ (±0.3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ND-G</td>
<td>2.4 (L)</td>
<td>6 (G or L)</td>
<td>10–100</td>
<td>25</td>
<td>obscured</td>
</tr>
<tr>
<td>ND-G/RDX150</td>
<td>13.6 (111)</td>
<td>34</td>
<td>2–100</td>
<td>150</td>
<td>1332.5</td>
</tr>
<tr>
<td>ND-G/RDX40</td>
<td>9.5 (111)</td>
<td>8.5 (110)</td>
<td>20–50</td>
<td>40</td>
<td>1332.5</td>
</tr>
<tr>
<td>ND-TNT/RDXw</td>
<td>4</td>
<td>6 (25 s.p.)</td>
<td>3–6, rare 10–100</td>
<td>120</td>
<td>1328.5</td>
</tr>
<tr>
<td>ND-TNT/HNSw</td>
<td>4</td>
<td>6 (25 s.p.)</td>
<td>3–6, rare 10–100</td>
<td>150</td>
<td>1328.5</td>
</tr>
<tr>
<td>ND-TNT/RDXd</td>
<td>4</td>
<td>7 (50 s.p.)</td>
<td>3–6</td>
<td>70</td>
<td>1328.5</td>
</tr>
</tbody>
</table>

Diamond (cubic), lonsdaleite, and graphite phases are denoted as D, L, and G, respectively. b s.p., secondary peaks.

Figure 5. Raman spectra of the samples ND-TNT/RDXw (spectrum 1), ND-TNT/RDXd, 6 nm sized fraction (spectrum 2), ND-TNT/HNSw (spectrum 3), ND-G/RDX40 (spectrum 4), and ND-G (spectrum 5) measured at room temperature in the range 1200–1700 cm⁻¹.
Table 3. Nitrogen Concentration Determined by Combustion Elemental Analysis and EELS, Results of EPR on the Presence of Ns and Relaxation Time Characteristics, and Results of FCS and ODMR on the Presence of NV Centers for Different Classes of ND

<table>
<thead>
<tr>
<th>sample</th>
<th>% N, elemental analysis</th>
<th>atomic N to C ratio, EELS</th>
<th>P1 (ppm)</th>
<th>$T_1$, ns</th>
<th>$T_2$, $\mu$s</th>
<th>presence of NV, confocal fluorescence</th>
</tr>
</thead>
<tbody>
<tr>
<td>ND-G</td>
<td>&lt;0.5</td>
<td>&lt;1%</td>
<td></td>
<td></td>
<td></td>
<td>present</td>
</tr>
<tr>
<td>ND-G/RDX150</td>
<td>&lt;0.5</td>
<td>&lt;1%</td>
<td></td>
<td></td>
<td></td>
<td>most pronounced, ~up to 3 centers in some 40 nm particle</td>
</tr>
<tr>
<td>ND-TNT/RDXw</td>
<td>2.54</td>
<td>3.1%</td>
<td>0.6</td>
<td>153</td>
<td>5.24</td>
<td>present</td>
</tr>
<tr>
<td>ND-TNT/HNSw</td>
<td>&lt;0.5</td>
<td>&lt;1%</td>
<td>&lt;0.006</td>
<td>100</td>
<td></td>
<td>present</td>
</tr>
<tr>
<td>ND-TNT/RDXd</td>
<td>2.61</td>
<td>5%</td>
<td>181</td>
<td>1.9</td>
<td></td>
<td>not detected</td>
</tr>
</tbody>
</table>

influenced by the phonon confinement effect and the diamond line position is actually not shifted from the 1332.5 cm$^{-1}$ position characteristic for the bulk material.

**N Content and State.** The nitrogen content in all samples was measured using a Carlo Erba EA 1108 CHNS Analyzer (combustion analysis). The data are summarized in Table 3. For the ND produced from a graphite precursor or a mixture of graphite with RDX, the nitrogen concentration was below the detection limit, i.e., below 0.5 wt %. The typical N concentration in the detonation ND produced from a mixture of TNT/RDX explosives is higher than 2 wt % (Table 3). The N concentration in ND produced from a mixture of TNT/HNS was also below the detection limit.

Normalized core-loss EELS spectra from the ND samples are shown in Figure 1S (Supporting Information). Nitrogen is detected in the samples ND-TNT/RDXd, ND-TNT/HNSw, and ND-TNT/RDXw; the nitrogen K-edge around 400 eV is clearly observed. Samples ND-TNT/HNSw and ND-TNT/RDXw only show a peak with maximum around 406 eV. This peak was previously attributed to the 1s $\rightarrow \sigma^*$ transition, indicating a tetrahedral (sp$^3$-like) incorporation of nitrogen. In sample ND-TNT/RDXd, a prepeak with maximum at 400.5 eV is present, related to the 1s $\rightarrow \pi^*$ transition, typical for nitrogen in a sp$^2$ configuration. While the N concentration in the samples produced from TNT/RDX mixture reach several percent (see Table 3), in the sample produced from a TNT/HNS mixture it is less than 1%, though a small peak is still detectable.

Pulsed electron paramagnetic resonance (EPR) in the X-band of microwave frequencies has been used to detect single substitutional nitrogen (P1 centers) and to estimate their concentration in the studied nanodiamond samples. The measured spectra are shown in Figure 6. The EPR signal from substitutional N was easily separated from the background, which is most likely related to surface defects, in the samples TNT/RDXw (spectrum 2) and graphite/RDX (spectrum 4). The background signal in the rest of the samples remained too strong to extract the P1 signal correctly even after pulse delay optimization (see Experimental Section). The concentration of P1 centers in the graphite/RDX sample was previously determined in ref 32 for W-band measurements. The P1 concentration in the TNT/RDXw sample was estimated using the sample graphite/RDX as a secondary standard. The very low P1 concentration in the TNT/HNSw sample allowed us to only make an upper-bound estimate of the P1 concentration (see Table 3). ESE EPR spectra measured at different time delays in the pulse sequences as described in the Experimental Section allow one to estimate spin—lattice relaxation time $T_1$ and spin—spin relaxation time $T_2$ (see Table 3).

A number of complementary studies provide integrated information about the nitrogen incorporation into nanodiamonds. Single particle fluorescence was investigated to gain insight into the photophysical properties of individual nanodiamonds. Individual nanocrystals were immobilized and investigated using home-built confocal/atomic force microscope combination. Figure 7 shows images of dispersed particles (AFM topography) and a fluorescence image of the same sample area. Nanodiamond particles produced from the graphite/RDX precursor as well as from TNT/RDX of dry and wet synthesis were analyzed. Remarkably, only crystals larger than approximately 20–40 nm show stable fluorescence corresponding to the presence of a NV defect. The largest content of luminescent particles was observed for ND produced from graphite/RDX, while in the detonation ND produced by dry synthesis no fluorescence was observed. ND-G/RDX150 (Figure 7A) contained a larger amount of fluorescing particles than the fractionated sample with smaller crystallite sizes (ND-G/RDX40). Optically detected electron spin resonance (Figure 7B,C) allows an unambiguous assignment of the fluorescence signal to the NV defect. From the measurements of photon statistics (second-order intensity correlation function) the maximum concentration of approximately 3 NV centers per particle for selected particles (Figure 7B) was estimated. It should be emphasized that on average, the number of NV centers is much less than content of substitutional nitrogen atoms. A spin—spin relaxation time $T_2$ of the NV centers formed during synthesis in the ND-G/RDX150 sample was approximately...
2 \mu s (Figure 7C). Fluorescence correlation spectroscopy analysis was also performed (Figure 2S, Supporting Information). Interestingly, no fluorescence related to the NV$^-$/C$_0$ centers was detected in the ND-TNT/RDXd sample produced from a mixture of explosives in dry cooling media. This is consistent with the confocal fluorescence/AFM results.

**DISCUSSION**

In situ production of optically active NV centers in nanodiamond particles during synthesis would be a very appealing approach, resulting in the large scale synthesis of photoluminescent NDs for numerous applications. Formation of NV centers requires the presence of substitutional nitrogen and vacancies in the diamond lattice. In ND synthesis using explosives, N is an integral part of the high-energy explosive compounds (Figure 1B). It can also be present as an impurity or an on-purpose dopant in graphite (or other carbon-containing materials) in the methods of the dynamic synthesis involving bulk carbon precursors for NDs production. Since the dynamic synthesis of NDs takes place under conditions far from equilibrium, it is expected that intrinsic point defects (vacancies) are formed and, depending on the cooling regime affecting their diffusion, can create complexes with nitrogen in the ND core.

Up to now, the N location in the diamond core was only comprehensively studied for NDs produced from a TNT/RDX detonation mixture.$^{5,28}$ The content of N in a typical DND core is approximately in the range of about 20000–30000 ppm (2–3 atom%).$^{5,28}$ It was concluded that one of the possible problems for producing luminescent detonation nanodiamonds is its high nitrogen content that does not allow production of active optical centers and significantly enhanced PL. The N atoms at high concentrations are possibly prone to the formation of complexes that are not optically active. In addition, at high concentrations, N atoms may suppress the optical activity of neighboring nitrogen atoms. Another possible barrier is the high density of twins and other coherent and incoherent grain boundaries in DND. A high density of grain boundaries in DND can promote enrichment and formation of nitrogen complexes$^{5,28}$ at these boundaries.

Hence, we assume that for the successful production of highly luminescent NDs of dynamic synthesis, the nitrogen content in the final ND product should be regulated by a proper choice of the precursor material. Recently, Pichot et al. demonstrated that the incorporation of melamine leads to a further increase by a factor 2 or 3 in the nitrogen content in the detonation nanodiamond core.$^{43}$ One way to decrease the overall N content in the precursor material is the addition of graphite (or another carbon material) to the explosives (sample ND-G/RDX, Table 3).
Another way to reduce the nitrogen content is using combinations of explosives with lower N content than in the TNT/RDX mixture. For example, a 50/50 mixture of TNT/RDX contains 21 atom % of N. In a 50/50 mixture of TNT and hexanitrostilbene (HNS, C$_{14}$H$_2$N$_6$O$_{13}$) (Figure 1B), there is 15 atom % of N. Indeed, in the samples produced from TNT/RDX nitrogen content is more than 2wt % while ND from the TNT/HNS mixture contains less than 0.5 wt % of N (Table 3). Substituting RDX with HNS significantly reduces the N content. It is also possible that the N−N units in the RDX composition (Figure 1B) contribute to enhanced N aggregation in the ND core, if they are not completely destroyed during detonation and are incorporated into the ND core as neighboring nitrogen atoms. These issues require further study though. Variations in the types of explosives can be used together with the addition of other carbon precursor materials (for example, combination of graphite and HNS) to achieve the desired result.

One can argue that oxygen is also a part of the composition of high-energy explosives, similar to nitrogen (Figure 1B) and can, in principle, be incorporated into DND core as well. In this regard we refer to the results by Koscheev et al. on thermal programmed mass spectrometry, which help reveal the elemental composition of the RDX surface and core. High temperature profiles (up to 1550 °C) of active gases released from RDX both under linear heating and under isothermal annealing demonstrate the presence of oxygen-containing gases (at temperatures below 800 °C), as well as hydrogen (peak at 900 °C) and nitrogen (peak at 1530 °C). On the basis of these thermal profiles, one can conclude that oxygen is released from the DND surface, while nitrogen is contained in the DND core.

The next question is the state of the incorporated nitrogen in the ND core. The pulsed EPR analysis (Figure 6, Table 3) demonstrates that N in a substitutional state is present in all NDs. The most pronounced substitutional nitrogen features are seen in ND produced from a graphite/RDX mixture (~0.6 ppm P1 centers). Previously, we have defined the N$_x$ content in this material to be approximately 1.2 ppm using pulse EPR in the W band. In this work the X band was used and values in the same order of magnitude for the N$_x$ content were obtained. In NDs produced from explosives, the N$_x$ content is 1−2 orders of magnitude lower (0.02 ppm and <0.006 ppm P1 centers in ND produced from TNT/RDX and TNT/HNS explosive mixtures, correspondingly). More pronounced N$_x$ satellites in the ND-G/RDX sample (Figure 6) can be attributed, in part, to the larger average crystal size for this type of the material (Figure 3). For these larger crystals with smaller specific surface area, background contributions from surface paramagnetic centers are far less pronounced (proportional to the $R^2$ (with $R$ being the radius of the nanoparticles)).

XPS, EELS (energy-loss near edge structure (ELNES)), and NEXAFS analysis provide information on the local N environment. The XPS spectra for N in UNCD films and in DND suggest the presence of two or, perhaps three types of N environment. Unique interpretation of the N XPS spectra in the C−N systems is not yet possible, but according to Titantah and Lamoën the observed features originate from nitrogen occupying two- and three-coordinated structures with at least one of the nearest neighbors being also a two- or three-coordinated carbon. This assignment corresponds well to the suggestion that N in UNCD and in DND is largely confined to grain- and intercrystallite boundaries and other extended defects and can, possibly, form N conglomerates. In the current work, EELS studies confirmed the presence of N at a level of several percent in NDs produced from a TNT/RDX mixture. Nitrogen is present in a sp$^3$ configuration in NDs of wet synthesis and in sp$^2$/sp$^3$ configurations in NDs of dry synthesis. This means that the NDs of a dry synthesis sample contain nitrogen incorporated not only into the diamond cores but also into the graphitic shell. Since the cooling stage for ND of dry synthesis lasts longer, a fraction of the nitrogen atoms may diffuse to the outer shells, which are in part graphitic as seen in HRTEM. The N concentration in the sample produced from TNT/HNS mixture was less than 1%. The N concentration in the samples ND-G and ND-G/RDX was below the detection limit of EELS.

Along with the presence of substitutional N in the ND cores shown in our study, NV centers are formed in different amounts in the various NDs. By use of a confocal fluorescence/AFM setup for analysis of individual NDs dispersed on a substrate, several individual fluorescent NDs were identified in different samples. The largest amount of luminescent NDs was observed in the unfractionated ND sample produced from the graphite/RDX mixture (ND-G/RDX150). These NDs have an average crystal size over 30 nm (Figure 3B). ODMR studies confirm that these centers are related to NV complexes (Figure 7B). It was estimated that a luminescent crystallite of ND-G/RDX150 may contain up to three NV centers. The PL from the NV centers was stable, without photobleaching. The total amount of grains containing PL centers was lower than that for typical HPHT NDs containing NV centers formed by irradiation and annealing. Compared to the results typically reported for single NV centers in bulk diamond or HPHT nanodiamond, the fluorescence intensity in the studied samples is relatively low, probably due to fluorescence quenching by numerous internal defects.

Preferential incorporation of the PL-active centers in larger crystallites was also observed for NDs produced from explosives under wet synthesis conditions. The role of the crystal size in forming NV centers during synthesis was confirmed by fluorescence correlation spectroscopy (Figure 2S, Supporting Information). Remarkably, no PL centers were observed in NDs produced from explosives under dry synthesis conditions. This was confirmed by investigation of NDs of dry synthesis produced by two different vendors. A possible reason for this observation is that in the dry synthesis method NDs remain at high temperature for a longer period of time, so that the defects responsible for the formation of the NV centers are annealed (diffuse to the surface). Again, this hypothesis requires further study.

Our work shows that preferential incorporation of nitrogen in a substitutional form into relatively big nanocrystals and subsequent formation of NV centers during synthesis is characteristic for various types of detonation-grown diamond. Preferential incorporation of nitrogen into relatively big nanocrystals was already reported for CVD growth conditions, as well as for detonation nanodiamond. Bradac et al. detected NV centers in individual 5 nm DND particles in samples produced from TNT/hexogen by the wet synthesis method. However, the luminescence exhibited intermittency depending on the local environment of the individual DND particles. While in the previous studies identification of nonblinking NV centers in detonation NDs was a rare event due to the small fraction of larger crystals, studies of NDs produced from graphite/RDX with an average crystal size of more than 30 nm showed the possibility of producing NDs containing significant amounts of the NV centers with measured spin−spin relaxation times of approximately 2 μs, large enough to be useful for applications.
The ultimate goal remains to produce the smallest possible nanodiamonds that contain NV centers. There is another class of recently discovered 1–2 nm in size hydrogen-passivated diamond clusters (diamondoids) in crude oil.\textsuperscript{30} Owing to the fact that these smallest diamond species are amenable to chemical synthesis and modification,\textsuperscript{51} chemical routes can be considered on synthesis of diamondoids containing substitutional nitrogen. Interestingly, intrinsic photoluminescence in the ultraviolet for adamantane has already been discovered\textsuperscript{52} and was attributed to recombination of self-trapped excitons. The inclusion of high amounts of nitrogen into the adamantane crystal lattice was however found to quench the luminescence.

\section*{CONCLUSION}

We performed a comprehensive study of different classes of NDs produced by detonation shock-wave-assisted synthesis. All experiments were performed using the same setups thus allowing a comparative analysis of the role of various parameters of the detonation synthesis on the nitrogen incorporation into the ND core and on the possible in situ formation of NV centers. On the basis of our observations, the following factors are important for enhancement of NV center formation: (i) the presence of a carbon precursor (graphite, carbon black, soot, etc.) mixed with a high energy explosive; (ii) the promotion of the formation of large \( \sim 30 \) nm crystals; (iii) the employment of fast cooling conditions promoting “freezing” of the formed NV centers (water cooling).

It is plausible that the molecular structure of RDX (two neighboring nitrogen atoms) promotes the formation of N aggregates in the ND core. It is thus possible that other high power explosives containing single N atoms in the molecule might be preferable (octogen, HNS). While crystal sizes in the studied NDs produced from a mixture of graphite/RDX are larger than those appealing for nanoscale magnetometry applications,\textsuperscript{14,15} they still can be useful in cell studies as luminescent probes or in nanocomposite materials as tracers of the NDs distribution. Important to note is that crystal sizes can be varied through variation of the composition of the precursor.\textsuperscript{23}

Our study clearly demonstrates that dynamic synthesis of NDs has a high potential for the production of highly desirable ND containing NV centers at an industrial scale.

\section*{EXPERIMENTAL SECTION}

Materials

(i) Nanodiamond produced by shock wave conversion of graphite to diamond was obtained from Microdiamant, Switzerland. According to the vendor specification, each diamond particle has a polycrystalline structure consisting of crystallites approximately 20 nm in size. Obtained product “DP 0-0.05µm” is an agglomerate-free slurry in deionized (DI) water with a mean aggregate size of 25 nm. This material is called ND-G in the paper, indicating graphite precursor for the production of ND. The elemental composition measured using a Carlo Erba EA 1108 CHNS analyzer was as follows: C, 90.4 wt %; H, <0.5 wt %; N, <0.5 wt %; O (the balance), 8.6 wt %.

(ii) The nanodiamond material produced by explosion of charges consisting of graphite and hexogen mixture (graphite + RDX) was obtained from Real-Dzerzhinsk, Russia. The material also possesses a polycrystalline structure, each particle consisting of a large number of nanosized monocrystalline blocks. This material is called ND-G/RDX in the paper indicating graphite mixed with RDX explosive material as a precursor for the synthesis of ND. ND-G/RDX150 and ND-G/RDX40 correspond to a slurry with average particle sizes of 150 and 40 nm, respectively. Sample ND-G/RDX40 is a fraction of sample ND-G/RDX150, obtained by centrifugation. Sample ND-G/RDX40 was further purified from residual sp\textsuperscript{2} carbon with a mixture of nitric/sulfuric treatment (1:3) before HRTEM, EELS, and confocal fluorescent microscopy studies. The incombustible impurity content in the ND-G/RDX150 product was 0.5 wt %. The elemental composition for ND-G/RDX 150 sample was C, 97.27 wt %; H, <0.5 wt %; N, <0.5 wt %; O (the balance), 1.7 wt %, and for ND-G/RDX40 sample C, 93.33 wt %; H, <0.5 wt %; N, <0.5 wt %; O (the balance), 5.7 wt %.

(iii) Detonation ND produced from carbon-containing explosives by detonation of at negative oxygen balance was obtained/purchased from New Technologies, Chelyabinsk, and Real-Dzerzhinsk, Ltd., Russia. Three types of DND were used according to the composition of the explosives mixture and a cooling method (wet/dry): ND-TNT/RDXw, ND-TNT/HNSw, and ND-TNT/RDXd. Sample ND-TNT/RDXw was synthesized by the detonation of a mixture of trinitrotoluene (TNT) and hexogen (40/60) in an ice cooling medium, followed by a soot purification process using a mixture of sulfuric acid with chromic anhydride, washing with DI water, and drying. Then the sample was additionally purified from metal impurities by boiling in a NaOH/H\textsubscript{2}O\textsubscript{2} mixture followed by washing in DI water, treating with ion-exchange resins, fractionating, and drying. The incombustible impurity content in the final DND product was 0.6 wt %. The elemental composition was as follows: C, 89.03 wt %; H, 0.96 wt %; N, 2.54 wt %; O (the balance), 7.5 wt %. The average aggregate size in a suspension of DI water was 120 nm. Sample ND-TNT/HNSw was produced from a mixture of trinitrotoluene/hexanitrostilbene (HNS) explosives in an ice cooling medium, followed by a soot purification process using a mixture of sulfuric acid with chromic anhydride, washing with DI water, and drying. The average aggregate size in a suspension of DI water was 180 nm. Sample ND-TNT/RDXd was synthesized by the detonation of a mixture of TNT and hexogen in a dry cooling medium consisting of gases, the products of the explosion reaction (predominantly CO\textsubscript{2}). It was purified from soot using singlet oxygen in NaOH and HNO\textsubscript{3} additionally treated in NaCl solution and fractionated to aggregates with average particle size 60 nm.

Transmission Electron Microscopy and Electron Energy Loss Spectroscopy. (High resolution) transmission electron microscopy (HR)TEM experiments were performed on a FEI Tecnai microscope operated at 200 kV with a point resolution of 0.20 nm.

Electron energy-loss spectroscopy (EELS) experiments were performed on a Philips CM30 microscope operated at 300 kV, equipped with a GIF-200 spectrometer. The EELS spectra were acquired using a convergence semiangle \( \alpha \) of 1 mrad, a collection semiangle \( \beta \) of 2 mrad, an energy dispersion of 0.3 eV per pixel and an energy resolution of approximately 1.2 eV. All core-loss spectra were background subtracted, deconvoluted, aligned using the onset of the carbon K-edge (at 284 eV), and normalized in intensity to their maxima. The nitrogen to carbon ratio (atom % nitrogen)
was obtained by model-based quantification of the acquired spectra. To model the core-loss spectra using the EELSMODEL software, a power-law background $AE^{-n}$ 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.

**XRD/SAXS.** The X-ray diffraction (XRD) pattern was acquired using Cu Kα radiation on a Panalytical X’pert diffractometer.

Small-angle X-ray scattering (SAXS) was performed using dedicated AMUR-K and SAXSees (Anton Paar) diffractometers. The size distribution of the scatterers was calculated assuming a spherical shape using the GNOM software.33

EPR. Measurements of pulsed EPR spectra were performed with Bruker Elexsys E580 (X-band) spectrometers at a temperature of 300 K. The pulsed EPR spectra were measured as an intensity of primary Hahn echo depending on the scanned magnetic field. A two-pulse sequence ($\pi/2 - \pi - \pi/2$) was used, in which the first pulse duration $\pi/2$ was 12 ns and the time delay $\tau$ between the pulses was optimized for each of the samples and varied within the interval 120–160 ns depending on the sample. The P1 center concentration in the samples (for which it was possible) was estimated by a secondary standard.

**Raman Measurements.** Raman spectra were recorded at room temperature using a LABRAM HR spectrometer with 488 nm excitation light from an Ar$^+$ laser. The laser beam was focused at a spot 2 μm in diameter on the surface of the DND samples. Specifically for the Raman study the samples were prepared in the form of a watery paste. It allowed excluding sample overheating even at 1 mW laser power whereas dry-powdered samples required a power as low as ~0.01 mW.

**Optical Microscopy and EPR Experiments.** Optical microscopy and atomic force microscopy of single diamond nanoparticles were performed using a home-built AFM/confocal microscope setup. Single diamond nanocrystals were excited by a diffraction limited focused laser beam. The Stokes shifted fluorescence was filtered from excitation light and used to detect metastable singlet state. Fluorescence correlation spectroscopy analysis was detected using software and hardware based on photon counting routine enabling us to study the statistics of the fluorescence emission on a time scale from a nanosecond to milliseconds.

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