Surface Chemistry and Properties of Ozone-Purified Detonation Nanodiamonds

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ABSTRACT: Nanodiamond from ozone purification (NDO) demonstrates very distinctive properties within the class of detonation nanodiamonds, namely very high acidity and high colloidal stability in a broad pH range. To understand the origin of these unusual properties of NDO, the nature of the surface functional groups formed during detonation soot oxidation by ozone needs to be revealed. In this work, thermal desorption mass spectrometry (TDMS) and IR spectroscopy were used for the identification of surface groups and it was concluded that carboxylic anhydride groups prevail on the NDO surface. On the basis of the temperature profiles of the desorbed volatile products and their mass balance, it is hypothesized that decomposition of carboxylic anhydride groups from NDO during heating proceeds by two different mechanisms. Other distinctive features of NDO in comparison with air-treated nanodiamond are also reported.

1. INTRODUCTION

Development of efficient methods of nanodiamond purification from detonation soot with low content of sp² carbon and small size of agglomerates combined with inexpensive, environmentally friendly technologies remains an important goal in the nanodiamond community. A gas-phase method of simultaneous purification and modification of detonation nanodiamond (DND) with ozone/air mixture has recently been developed.1−3 The technology uses a fluidized bed reactor fed with air enriched with ozone, accompanied by thorough mechanical and gas stream mixing of the soot. In the reactor, the nondiamond byproduct of detonation synthesis, mostly sp² amorphous and graphitic carbon, react with ozone at the elevated temperature and are converted to CO₂ or CO. This gas-phase purification is an attractive alternative to the more commonly used method of detonation soot treatment with concentrated acids or other strong liquid oxidizers, which make up to 40% of the product cost. For instance, for the production of 1 kg of DND from soot containing 40 wt % DND, 35 L of concentrated sulfuric and nitric acid (85:15) are required, in combination with treatment at high temperature.4 In contrast, the technology of purification with ozone is more environmentally friendly and may find broad application in nanoparticle-related industry. It is important, however, to remember that ozone is toxic and aggressive and destruction of residual ozone after treatment requires special precautions (which are, however, well-known in the field).

Ozone-modified nanodiamonds were found to have a number of distinctive characteristics. NDO-based suspensions possess high colloidal stability in the range of pH 2−12,5 far exceeding a pH range of stability for other types of nanodiamonds produced from carbon-containing explosives. The Z-average size of polydispersed NDO in their water suspensions is about 160−180 nm (corresponding volumetric size 120 nm), as measured by dynamic light scattering. This number is the smallest average size reported for commercially available, unfractionated, polydispersed DNDs. In addition, the content of the primary polyhedral-shaped, faceted particles with a size of 3−5 nm in the polydispersed NDO is substantially higher than that of the acid-purified DNDs.5 Polydispersed NDO hydrosols were found to possess extremely low values of pH (pH ∼1.6 for 10% NDO suspension in water2) and featured a constant zeta potential (∼45 mV) over a wide pH range of 2−12,5 apparently due to the enrichment of the surface with oxygen-containing strong-acid groups.

Polydispersed NDO material forms stable (for at least 4 years) hydrosols with ND content up to 20 wt %. NDO also forms stable suspensions in a wide variety of organic solvents: alcohols (methanol, ethanol, isopropyl alcohol), acetone, methyl methacrylate, oils,
N-methyl-2-pyrrolidone, and other solvents. It should be noted that highly iridescent photonic crystals formed by diamond particles have been observed only for NDO, indicative of its high purity from nondiamond carbon and high surface charge preserving ordered arrangement of NDO aggregates in a suspension at certain concentration of nanoparticles.

Recently, results of FTIR, NMR, and XPS investigations of polydispersed NDO have been reported, identifying the presence of radicals at the DND surface. The high density of reactive surface groups and radicals can be used in a wide variety of composite materials, for example for formation of bonds of radicals with polymer molecules without additional modification of the nanodiamond surface (esterification, amidation, and other bonding), as intermediate structures for consequent reactions of the surface groups and for formation of fillers in polymers and nanoparticles for use in biotechnology, cosmetics, and medicine (attachment of biomarkers, adsorption of biomolecules, capture of free radicals (serving as antioxidants), and toxins and other applications). Because of the high density of highly reactive groups, further functionalization of the nanodiamond material in the desired direction is facilitated. It was also observed that NDO annealed in vacuum produces onionlike carbon with a smaller size and narrower size distribution than acid-purified DND. However, there is still uncertainty over the identification of surface oxygen- and nitrogen-containing groups responsible for highly acidic properties of NDO.

Oxidation of nondiamond carbon is also possible by treatment of samples in air, at 350–450 °C, without presence of ozone. This increasingly popular method requires less precaution in terms the disposal of harmful gases, but the treatment temperature is higher. We will show in the article that the resulting materials also exhibit distinctive features, as is the case for example NDO.

In the current study, we extend the investigation of the surface groups on NDO to the method of thermal desorption mass spectrometry (TDMS), which allows us to determine the presence of oxygen-containing groups with high accuracy. We also provide semiquantitative estimates of the density of acidic surface groups on NDO. From a practical point of view, we provide a comparative analysis of the efficiency of fractionation of NDO and ND oxidized in air, demonstrating that a fraction with smaller size and higher yield of the smallest particles can be extracted from NDO. The reported results emphasize the uniqueness and practical value of the ozone purification method.

2. EXPERIMENTAL SECTION

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 at VNITTF, Snezinsk, Russia. DND content in the soot was 70 wt %. Prior to the treatment in the ozone purification reactor, the soot was depurified of metal contaminants by washing with acids at ambient temperature, followed by a washing in DI water and drying. Incombustible impurities content in the soot was 0.5 wt %. The ozone purification treatment of the detonation soot was carried out at 150–200 °C over 72 h. Incombustible impurities content in the NDO was 0.8 wt %. After ozone purification, the resulting NDO powder had light-gray color. Its ignition temperature is 450 °C.

Sample NDO-80 is a black-colored fraction of the NDO sample (obtained by centrifugation) with a zeta-average size of 80 nm (volumetric size 40–50 nm). Nanodiamonds used for a comparative study with NDO were obtained from the same soot and were treated as follows:

(i) Sample NDS was purified from nondiamond carbon by oxidation of the detonation soot with a solution of chromic anhydride in sulfuric acid. The next steps in the purification included multiple washing cycles with DI water, treatment with ion-exchange resins, washing, and drying.

(ii) Sample NDA was obtained by heating of NDS in an oven (flow air ambient) at temperatures above 400 °C for an hour, as described in (12).

(iii) Sample ND-H was obtained by treatment of NDS in hydrogen flow at 400 °C for 6 h.

(iv) Industrial sample RUDDM1 with negative zeta potential used for comparative studies was purchased from RealDzerzinsk, Inc., Russia.

In fractionation experiments, ND was dispersed in DI water using a direct-immersion horn-type ultrasound sonicator (output power of 100–400 W). The ND hydrosols were centrifuged at 20 °C using a multipurpose centrifuge (Thermo Electron IEC Multi RF Refrigerated Centrifuge) equipped with a 17.5 cm fixed angle rotor and 50 mL conical centrifuged tubes.

ND particle-size distributions in the hydrosols were measured by the dynamic light scattering technique using a Malvern Zetasizer (Malvern Instruments Ltd., UK) particle-size analyzer. The Zetasizer was also used for electrophoretic mobility measurements. Zeta potential was derived from the measured electrophoretic mobility using the Smoluchowski’s approximation for Henry’s function, the latter equals 1.5. This is justified by a relatively large size of the particles. Because the coefficient of proportionality is known, electrophoretic mobility can be easily recalculated from the reported data on zeta potential. Viscosity and dielectric constant of the slurry were assumed equal to that for DI water at 25 °C. Conductivity of DI water used in experiments was 18 MΩ cm. All measurements were done at ND concentration 0.1 wt %. After dispersion of 0.1% NDO in DI water it provides conductivity of the slurry approximately 0.03–0.05 mS/cm.

For the TDMS analysis, a portion (2.0 mg) of as received ND powder was placed into a Ni-envelope (precleaned ultrasonically in acetone and water and dried) and introduced in the high-temperature vacuum oven. The sample was then degassed under evacuation by ion pump for one day at room temperature. The residual pressure at the end of degassing was in the range 10−7 Torr.

TDMS analysis was performed by continuously measuring the mass spectra of gases released from the sample under programmed heating with constant rate 16 °C/min up to 1150 °C. Mass spectra were recorded by means of a quadrupole mass spectrometer MX7304 (“Electron”, Sunny, Ukraine) in the range of mass numbers 10–105 amu (up to 700 °C) and 2–50 amu (700–1150 °C). MS scan rates allow measuring the temperature profiles of released species with a temperature resolution no better than 12 °C. The evolved gases were pumped permanently at a rate of ∼1 L/s (relative to nitrogen). In this case, the measured partial pressures of the gases were proportional to the desorption rates at every moment. The total pressure in the vacuum chamber during heating was measured by an ionization gauge.

The obtained mass spectra (more than 100) were analyzed and handled by means of special homemade software.
3. RESULTS AND DISCUSSION

3.1. TDMS and FTIR of NDO, NDA, and NDS Samples.
Typical main products of thermal desorption from the surface of detonation ND are H₂O (100–600 °C), hydrocarbons (200–400 °C), CO₂ (200–600 °C), CO (400–1000 °C), and H₂ and HCN (above 800 °C). Thermal programmed desorption (TPD) curves for the main ion fragments in the mass spectra of volatiles desorbed from surfaces of NDO, NDS, and NDA samples measured at the same conditions are shown in Figure 1. NDO and NDS samples also demonstrated the presence of SO₂ traces and hydrocarbons (spectra not shown). The concentration of hydrocarbons in NDS was substantially higher in comparison to NDO, likely in part due to a more efficient oxidation of hydrocarbons with ozone and in part due to the purification of NDS with ion-exchange resins. It can be seen from Figure 1 that the samples after gas-phase treatment with ozone, thermal treatment in air, and acid purifications of the detonation soot have significantly different intensities and shapes of the temperature profiles for the desorption of all major species.

CO and CO₂ were the dominant species in the products of thermal desorption. The desorption profiles of CO and CO₂ species formed as a result of the thermal destruction of surface oxygen-containing groups are of special interest. From these profiles, it is possible to reconstruct the structure of the oxygen-containing groups and explain a significant difference in the properties of the NDO and NDS samples. The larger the degree of surface oxidation, the lower the temperature of the CO desorption maximum, and the larger the amount of desorbed carbon oxides. These features are clearly seen for NDO sample (Figure 1) oxidized with ozone, one of the strongest oxidizers.

The results of the deconvolution of the TPD curves for CO and CO₂ for the NDO, NDA, and NDS samples are illustrated in Figure 2. Possible assignments of the main peaks for NDO sample are as following: \(^{13,14}\) peaks 390–460 °C (CO₂ only) – carboxylic and lactone groups; peak 530 °C (CO₂ + CO) – cyclic acid anhydride species; peak 680 °C (CO only) – ether and phenol groups. Decomposition of anhydride groups should produce the equal amounts of CO₂ and CO molecules as it was observed for different carbon materials. \(^{15,16}\) However, in the case of NDO the desorption intensity of CO species at 530 °C is more than twice that for CO₂ species (the ratio CO/CO₂ was calculated from mass spectra taking into account the difference in sensitivity of MS and in pumping rates of CO and CO₂), requiring an assignment of these additional CO species. A temperature of 530 °C is too low for desorption of ether or carbonyl (keton) species. Therefore, it can be assumed that the additional CO species desorbed at 530 °C originate from partial decomposition of complex molecular compounds, part of which were released at lower temperatures (as the CO₂ peak at 460 °C, Figure 3).

To have a correct mass balance of the desorbed CO and CO₂ species associated with specific functional groups, it can be hypothesized that a fraction of anhydrides decompose in a two step process at two different temperatures (Figure 3). For example, a partial decomposition of anhydrides takes place by desorption of CO₂ species at peak temperature 460 °C, whereas the CO part of the anhydride groups is desorbed at a peak temperature 530 °C. At the same time, desorption of another fraction of anhydrides from the diamond surface proceeds with the simultaneous removal of both CO and CO₂ species at a peak temperature 530 °C. The existence of several mechanisms of

![Figure 1. Comparison of TPD spectra of the main desorbed gases for the NDO (dashed lines), NDS (dotted lines), and NDA (solid lines) measured at the same conditions. Spectra were normalized to the sample weight.](Image 60x396 to 285x733)
Figure 2. Results of deconvolution of the TPD curves for CO and CO$_2$ using a multiple Gaussian function for NDO (a), NDS (b), and NDA (c). The profile for CO was corrected for the contribution of CO$^+$ fragments from the CO$_2$ signal.
removed from the surface. Facets with low Miller indexes are denoted. 3-coordinated carbon surface atoms. 1-coordinated atoms had been removed from the DND surface can be due to di-anhydrides from ND surfaces corresponding to thermal desorption from DND surface. The dehydration of two adjacent carboxylic acid groups on ND surface is observed in the 100–600 °C range at a low rate. Even if we assume that all these desorbed H2O are from two adjacent COOH groups, the whole amount of desorbed H2O is more than 1 order of magnitude lower than the amount of CO and CO2 desorbed due to anhydride decomposition (the estimation was made using the data of part a of Figure 2 taking into account the sensitivity of MS to different gases). Hence, the input of COOH transformation to anhydride formation in the course of programmed heating in TDMS measurements should be very small compared to the amount of pristine anhydride groups.

For sample NDS, the main TDMS peaks are assigned as follows: peaks 310–415 °C (mainly CO2) — carboxylic groups; peak 560 °C (CO2 only) — lactone groups; peak 690 °C (CO only) — ether and phenol groups; peak 800 °C (CO only) — carbonyl groups. The main oxygenated surface species in NDS are carbonyl groups. A very low abundance (if any) of cyclic acid anhydride groups is observed in this sample.

For sample NDA (Figures 1 and 2), the main features of CO and CO2 desorption profiles can be interpreted as follows: peak CO2 near 470 °C (CO2 only) — lactones and partial decomposition of anhydrides (mechanism 1); peaks CO and CO2 near 570–590 °C — decomposition of anhydride groups (mechanism 2); peak near 660 °C (mainly CO) — ether and phenol groups; peak 760 °C (CO only) — carbonyl groups. Sample NDA (in contrast to NDO) showed a high concentration of carbonyls close to that observed in NDS. Another important difference — the amounts of CO and CO2 desorbed simultaneously in the range of anhydride peak for the sample NDA, have similar values and are very close to the amount of desorbed CO2 for NDO. The amount of CO2 desorbed from NDA near 460 °C was much smaller compared to the case of NDO. The anhydride peak for NDA was shifted to ~580 °C compared to 520 °C for NDO. These results indicate that even though the high-temperature air oxidation gives rise to the surface anhydrides, ozonation leads to larger amount of anhydrides on ND surface and results in the appearance of a new type of anhydride groups, decomposed in a two-step mechanism as described above.

The ozone treated ND does not contain carbonyls that are present in NDS and NDA and decomposed near 800 °C according to TDMS data (Figure 2). The simple oxidation of ND in air at temperatures up to 450 °C did not decrease the high temperature release of CO due to carbonyl decomposition (Figure 5 in ref 13). Moreover, we have found by TDMS that the thermal oxidation of ND preliminary annealed in vacuum at 1100 °C (all surface groups removed) lead to the reappearance of carbonyls. This means that in contrast to thermal oxidation by oxygen the ozone treatment does not generate carbonyl groups on ND. Moreover, one could suggest that the carbonyl groups on the ND surface are transformed to other more acidic groups upon ozone attack, as was observed for ozonated activated carbon by means of XPS.

FTIR spectra for both samples are displayed in Figure 5. The results of the deconvolution of the part of FTIR spectra for NDO and NDS samples are illustrated in parts b and c of Figure 5 correspondingly. In contrast to the NDS sample, there is no

![Figure 3](image-url) Illustration of the possible desorption mechanisms for anhydrides from ND surfaces corresponding to thermal desorption peaks at two different temperatures.

![Figure 4](image-url) Illustration of a 4.2 nm diamond particle with a near-spherical morphology. Purple and green colored atoms correspond to 2- and 3-coordinated carbon surface atoms. 1-coordinated atoms had been removed from the surface. Facets with low Miller indexes are denoted.
The 1720 cm\(^{-1}\) band (carbonyl structures within surface groups of low degree of oxidation) present for NDO. The main band in NDO is 1858 cm\(^{-1}\) (cyclic acid anhydride structures), whereas bands at 1787 cm\(^{-1}\) (lactone) and 1670–1620 cm\(^{-1}\) (hydroxyls) are also present. The position of CO-band in FTIR spectra of ozonated ND has an extreme value (1850 cm\(^{-1}\)) compared to other types of ND.\(^{13}\) The same band (1857 cm\(^{-1}\)) was observed for ozonated carbon black.\(^{19}\) These data indicate a unique state of oxidation of the ND surface caused by ozonation at elevated temperatures. This state cannot be achieved by ordinary thermal oxidation of ND in oxygen at any temperatures. Moreover, the additional treatment of ozonated ND in air at 450 °C caused a shift of the CO-band from 1850 to 1810 cm\(^{-1}\) removing the specific features of ozonated ND (the CO-band looked the same after thermal treatment in air for all ND samples independent of their initial oxidation state).\(^{13}\)

Reactions of \(O_3\) with different carbonaceous materials such as carbon black,\(^{19,21}\) charcoal,\(^{20}\) micrographite,\(^{21}\) carbon nanotubes,\(^{22}\) fullerenes,\(^{21}\) ethylene\(^{19}\) have been the subject of extensive research. The reaction between ozone and carbonaceous species involves two stages: the gasification of the surface to CO and CO\(_2\) and its functionalization with oxygenated chemical groups, mainly COOH but also presence of carboxylic acid anhydrides and lactones is well documented.\(^{15–22}\) Smith et al. discussed formation of carboxylic acid anhydrides during interaction with ozone followed by reaction with water producing two COOH groups.\(^{24}\) The mechanism of formation of the anhydrides as a result of the reaction between 3 oxygen atoms and 2 carbon surface atoms, however, was not elaborated. In the experiments where carbon samples were treated with ozone under anhydrous conditions, a direct mechanism of COOH groups formation was suggested, involving surface C–H bonds.\(^{25}\) A model reaction of this system is the ozone–ethylene reaction involving cleavage of C=\(\equiv\)C double bonds.\(^{23}\) In this case, the unstable primary ozonide is formed in a first stage, giving rise to more stable secondary ozonide. The oxygenated groups are formed during the rupture of this secondary ozonide. This mechanism was used to explain the increase of the content of acidic groups (carboxylic, lactone) on the surface of activated carbon under ozonation.\(^{16,25}\) The model reaction of ozone with polyaromatic hydrocarbons was used to explain the appearance of anhydride species on the surface of carbon black during ozonation at elevated temperatures.

Figure 5. FTIR spectra (reflection mode) of NDO and NDS (a); results of deconvolution of the part of FTIR spectra (2000–1600 cm\(^{-1}\) range, corrected for the baseline in this region) for NDO (b) and NDS (c).
Figure 6. a) Background subtracted, normalized core-loss carbon K-edge EELS spectra of samples NDO-80, NDO and NDH. The fine structures mainly show a diamond $\sigma^*$ (sp$^3$) contribution at 292 eV and a small $\pi^*$ (sp$^2$, sp) contribution at 285 eV. Nitrogen is detected in all samples through the K-edge with maximum at 406 eV. b) Typical DND particle in sample NDO showing the presence of a [111] twin plane indicated by an arrow. The FFT of the nanoparticle evidence the [011] zone axis orientation, as well as the twinning over a [111] twin plane through a mirroring of the FFT (mirror plane indicated by two arrows perpendicular to the twin plane in real space) The main surface facets of the DND particles are {111} and {100}-like and show only a minimal presence of non-sp$^3$ carbon. c) Large, multiply twinned DND particle. The surfaces of the DND particles show only a minimal presence of non-sp$^3$ carbon.

temperature (400 K) through formation of hydroxyls at first stage, followed by a transformation into carboxylic acid species, yielding anhydride groups.$^{19}$ So, the formation of carboxylic groups on the surface of carbon materials is explained and presence of acid anhydride is well documented.

In our work, the ozonation of ND was performed at elevated temperature. The high concentration of surface anhydrides can be explained in this case by dehydration of two adjacent COOH groups formed during ozonation. However, the direct production of anhydride groups cannot be excluded as it is known that the ozonolysis of alkynes could give an acid anhydride.$^{26}$

The special features of ozonated ND indicating the presence of anhydrides, namely the simultaneous desorption of CO and CO$_2$ near 500 °C in TDMS measurements and IR-absorption band above 1800 cm$^{-1}$, as well as the other features of TDMS and FTIR spectra, were stable for at least 5 years storage in laboratory conditions without special precautions (the first measurements were done a month after sample preparation). So, we have no evidence for any long-term influence of NDO storage in laboratory environment on the anhydrides on the surface of ND. We can conclude that the rate of possible reaction of the moisture in air with surface anhydrides (forming carboxylic acid) is very low in our ozonated sample. A possible reason for high stability of acid anhydrides on DND can be a high density of the carbon sites on the diamond surface, preventing conversion of acid anhydride functionality into two COOH groups due to steric hindrance. When NDO is dispersed in water media, however, steric hindrance is not essential due to ionization of the COOH groups.

3.2. EELS and HRTEM. A comparative analysis of the purification of DND from nondiamond carbon using a variety of oxidation and reduction reactions was recently performed.$^{27}$ Of all the DND samples (including treatment with ozone-, air-, fluorine, hydrogen, and reduction with LiAlH)$_4$, samples NDO, NDO-80, and ND-H were the samples with the cleanest surfaces (almost free of sp$^2$ carbon). This was evidenced by electron energy-loss spectroscopy (EELS) and also by high-resolution transmission electron microscopy (HRTEM) for the case of sample NDO. Using the fine structure of the carbon K-edge in a typical EELS spectrum, the presence of graphitic sp and sp$^3$ bonded carbon can be determined.$^{28}$

EELS carbon K-edge spectra for samples NDO-80 (80 nm fraction of NDO), NDO and NDH are displayed in part a of Figure 6. All spectra are aligned to the carbon K-edge onset at 284 eV. The spectra show typical diamondlike ($\sigma^*$) energy-loss near edge structures (ELNES) starting at 292 eV. The spectra also show a small carbon prepeak (varying from sample to sample), typical for graphitic sp or sp$^2$ bonded material at 285 eV ($\pi^*$ contribution). NDO-80 shows the lowest content of graphitic ($\pi^*$) material through the prepeak to the carbon K-edge at 285 eV, indicating that the surface of sample NDO-80 are extremely clean. Samples NDO and ND-H demonstrate a slightly higher graphitic surface content (although the amount of non-sp$^3$ carbon in these samples remains very low). Possibly sp$^2$ carbon is confined within intercrystallites regions within large aggregate and is inaccessible for ozone. Both NDO samples show the presence of traces of oxygen at 532 eV (not displayed), but the signal is stronger for sample NDO (180 nm) than for sample NDO-80. Earlier XPS studies of ozone-purified DND also revealed the absence of sp$^2$ carbon at the surface of the diamond nanoparticles.$^5$
To illustrate the extremely low graphitic content at the crystal surfaces, two examples of DND particles from sample NDO are displayed in parts b and c of Figure 6. All HRTEM imaging is performed at lowered acceleration voltage (80 kV) in an aberration corrected instrument, allowing the surface of the particles to be imaged in great detail while minimizing the risk of surface graphitization by knock-on damage due to illumination under the electron beam. In part b of Figure 6, a typical 6 nm DND particle is displayed. The main surface facets are \{111\}-like, with some \{100\} truncation present. The particle shows the presence of a single \{111\}-type twin plane, which is often seen in DND material. The surface facets can be seen to be almost free of non-sp\(^3\) carbon. This is also the case for the larger multiply twinned nanoparticle displayed in part c of Figure 6. Almost all surface facets are \{111\}- or \{100\}-like and are almost free of graphitic material.

### 3.3. Estimates of the Amount of O Groups on NDO Surface

Several methods of analysis can be used for experimental determination of the composition and amount of surface groups, for example polarography, titration, Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), thermo-desorption mass spectrometry, reaction with metallic potassium,\(^{29}\) and other methods.

Of particular interest is an estimate of a maximum possible coverage of a DND particle surface by oxygen-containing groups. Such an estimate can be performed most accurately using atomistic modeling. An atomic model of 4.2 nm diamond particle was constructed with a near-spherical morphology (Figure 4). 1-coordinated atoms have been removed from the surface. The total number of carbon atoms is 7157, the amount of surface atoms equals 1122 (15.7 atom %); 744 of these surface atoms are 3-coordinated atoms and 378 atoms have two dangling bonds.

A nanodiamond particle with near-spherical morphology has multiple low-index facets, such as \{001\}, \{011\}, and \{111\} types, exposed at its surface (Figure 4). In the estimates of the maximum possible amount of oxygen-containing groups, the possibility of surface reconstruction of nanodiamond particles (dimerization of \{001\} surface) has been taken into account, leaving only single radical sites on the surface of the particle. The amount of surface coverage by several types of characteristic surface groups was assigned (2 and 1.5 oxygen atoms per carbon surface site for carboxylic and anhydride groups, correspondingly) and resulting elemental composition for the particle was calculated. Carbon atoms remaining unbound after placement of oxygen-containing surface groups were saturated with hydrogen atoms.

### Table 1. Examples of Elemental Composition of a Nanodiamond Particle 4.2 nm in Size Depending on the Type of Surface Groups and a Fraction of the Surface of a Particle Occupied by Different Surface Groups\(^{a}\)

<table>
<thead>
<tr>
<th>surface composition</th>
<th>C (diamond core), mas.%</th>
<th>H mas.%</th>
<th>O mas.%</th>
<th>C (surface groups) mas.%</th>
<th>C, total mas.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% – H</td>
<td>98.7</td>
<td>1.3</td>
<td></td>
<td></td>
<td>98.7</td>
</tr>
<tr>
<td>100% – OH</td>
<td>81.9</td>
<td>1</td>
<td>17.1</td>
<td></td>
<td>81.9</td>
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<tr>
<td>50% – OH</td>
<td>89.5</td>
<td>1.2</td>
<td>9.3</td>
<td></td>
<td>89.5</td>
</tr>
<tr>
<td>50% – H</td>
<td>77</td>
<td>1</td>
<td>16</td>
<td>6.0</td>
<td>83</td>
</tr>
<tr>
<td>50% – COOH</td>
<td>88.6</td>
<td>1.16</td>
<td>7.4</td>
<td>2.8</td>
<td>91.4</td>
</tr>
<tr>
<td>50% – H</td>
<td>80.5</td>
<td>0.52</td>
<td>12.6</td>
<td>6.3</td>
<td>86.8</td>
</tr>
<tr>
<td>20% – anhydride</td>
<td>90.5</td>
<td>0.94</td>
<td>5.7</td>
<td>2.9</td>
<td>93.4</td>
</tr>
<tr>
<td>80% – H</td>
<td>82.8</td>
<td>0.72</td>
<td>11.6</td>
<td>4.6</td>
<td>87.2</td>
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<tr>
<td>ND aggregate</td>
<td></td>
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<td></td>
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<tr>
<td>H = 33.4%</td>
<td></td>
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</tr>
<tr>
<td>COOH = 33.4%</td>
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<td>GB = 22.2%</td>
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</table>

Areas with sp\(^2\) C on \{111\} facets — 11%  

\(^{a}\) In the last line of the table, an example of a tightly bound aggregate (\(~20 \text{ nm in size}\)) is provided. Abbreviation: GB — grain boundaries. It is assumed in the calculations that 0.5 mass% of nitrogen is located in the nanodiamond core.
groups (when steric effect, in general, can be avoided), the oxygen content is about 16 wt % and 12.6 wt % correspondingly in the overall ND composition. The steric hindrance for surface coverage by anhydride groups can be avoided even at higher surface coverage, about \( \frac{2}{3} \) (66.6\%) in such model 2 nearest neighbor carbon surface sites are bonded to the anhydride group and a third carbon terminating a surface is bond to H atom). For \( \frac{2}{3} \) of the surface coverage by anhydrides, the oxygen content is about 15.7 wt % in the overall ND elemental composition, similar to 50% coverage by carboxylic groups.

The possibility of aggregate formation (densely packed primary particles connected by covalent bonds) was also included in the calculations. Approximately 22% of ND carbon surface atoms participate in the formation of grain boundaries (GBs) between densely packed particles. Buckyfication of the surface (transformation of (111) planes into sp^2 shells)\(^{30}\) was also taken into account. On the basis of the total surface of exposed (111) planes, it was estimated that total 11% of carbon sites located on the surfaces (Figure 4) can participate in the formation of sp^2 shells. Taking into account that a total fraction of 33% of carbon surface sites is not available for bonding with functional groups due to aggregation, the remaining sites were redistributed between carboxyl groups and hydrogen (Table 1, last line). In this case, the oxygen content is approximately 11.6 wt % in the overall ND composition.

The calculated content of C, H, N, and O is in a good agreement with content of these elements defined from a standard method of spectroscopic analysis of the sample during combustion (using, for example, a Carlo Erba CNS Elemental Analyzer). For example, in one of the batches of the NDO material the composition is as following: C 83.8 mas.%, H 0.3%, N 2.3%, incombustible impurities 0.5 mas.%, oxygen — the rest (13.1%)). On the basis of the estimates in Table 1 and experimental elemental analysis, it can be concluded that more than 30% of the surface of the tight aggregates of nanodiamond particles can be occupied by oxygen-containing groups. To use the estimates from Table 1, it is important that DND sample is well purified from nondiamond carbon. Sp^2 carbon species have high surface area, can be easily terminated with oxygen, and thus cause a misinterpretation of the results of the elemental analysis of nanodiamond. For example, some soot samples can contain a high amount of oxygen.\(^{31}\)

One more estimate of the fraction of the NDO surface occupied by oxygen-containing groups with acidic properties was done based on the measurement of the size of aggregates and pH of a 10 wt % hydrosol of nanodiamond material. An amount of the protonated groups per unit area affecting the pH was estimated. The average aggregate size of the nanodiamond of the present example purified from soot using ozone was 140 nm, according to the method of dynamic light scattering. The pH of a 10 wt % hydrosol of this nanodiamond is 1.6. The amount of surface groups with acidic properties per unit area of this nanodiamond varies between 5.3 and 8.8 groups/nm^2 depending on the assumed density of the aggregates of the primary particles; the density assumed in these calculations is 1.5 g/cm^3 for loose aggregates and 2.5 g/cm^3 for densely packed aggregates. For the aggregate size of 140 nm, the fraction of groups with acidic properties formed from oxygen compounds occupies from 28% up to 46% of the surface of nanodiamond particles (based on known average density of carbon atoms on a surface of nanodiamond particles (approximately 18.9 atoms/nm^2)).

### Table 2. Results of Fractionation Using Different Centrifugation Regimes and Different Types of Nanodiamonds

<table>
<thead>
<tr>
<th>fraction number</th>
<th>centrifugation regimes (g-forces)</th>
<th>NDA-425C, D (nm)</th>
<th>NDA-415C, D (nm)</th>
<th>NDO, D (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>polydispersed powder</td>
<td></td>
<td>210</td>
<td>250</td>
<td>180</td>
</tr>
<tr>
<td>1</td>
<td>1000</td>
<td>370</td>
<td>360</td>
<td>470</td>
</tr>
<tr>
<td>2</td>
<td>3000</td>
<td>255</td>
<td>242</td>
<td>273</td>
</tr>
<tr>
<td>3</td>
<td>5000</td>
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<td>205</td>
</tr>
<tr>
<td>4</td>
<td>8000</td>
<td>164</td>
<td>197</td>
<td>170</td>
</tr>
<tr>
<td>5</td>
<td>10000</td>
<td>138</td>
<td>173</td>
<td>142</td>
</tr>
<tr>
<td>6</td>
<td>12000</td>
<td>111</td>
<td>145</td>
<td>114</td>
</tr>
<tr>
<td>7</td>
<td>20000</td>
<td>103</td>
<td>133</td>
<td>109</td>
</tr>
<tr>
<td>8</td>
<td>supernatant</td>
<td>60</td>
<td>90 (low%)</td>
<td>58</td>
</tr>
<tr>
<td>8*</td>
<td>25000</td>
<td>82</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>supernatant</td>
<td>53</td>
<td>43</td>
<td></td>
</tr>
</tbody>
</table>

*Fractions 1-7,8* — residue re-dispersed in DI water; fractions 8,9 — supernatant; the centrifugation time for every fraction is 5 minutes, excluding fraction 1 for which the centrifugation time was 3 minutes; D — Z-average size of the aggregates in a fraction (nm).

**Figure 8.** Diagram of yield of the fractions after consequent centrifugation of initially polydispersed nanodiamond material of ozone purification and nanodiamonds after acid-chromic anhydride purification followed by modification through heat treatment in air at 415 °C (NDS-415C) and at 425 °C (NDS-425C) for 1 h.

### 3.4. Fractionation Experiments and Zeta Potential of NDO.

An important characteristic of an industrial DND material after soot purification is the size of the aggregates of the primary particles. Specifically, average aggregate size in as-received material as well as content of primary particles and small-sized aggregates after fractionation by centrifugation, for example, are of interest. At the present time, many efforts are directed toward decreasing the sizes of aggregates of detonation nanodiamonds in suspensions. Typical average aggregate sizes (Z-average) of polydispersed nanodiamonds from different vendors are within the 250—400 nm range.

The average size of the as-received from soot polydispersed NDO material is noticeably smaller: 180 nm and less, depending upon regimes used for the gas-phase thermal treatment. Correspondingly, the fraction of primary particles and aggregates of small sizes extracted by fractionation from the initial polydispersed material for the NDO material exceeds the amount of primary particles and small aggregates extracted by centrifugation.
at the same conditions from polydispersed nanodiamond material purified and modified by other known methods (including the method of heat treatment in air flow7–12 (without addition of ozone)). As an illustration, the polydispersed NDO material and nanodiamond purified from the soot using acidic treatment and then additionally modified by treatment in an air flow at 415 and 425 °C were fractionated by centrifugation in similar conditions (Table 2, Figure 8). As can be seen from Figure 8, the amount of the small-sized fractions of the material after ozone purification/modification is significantly higher in comparison to the fractionated nanodiamond samples after oxidation in air. This is due to the fact that, after purification using ozone, necks between primary particles within aggregates are significantly etched and thinned so that during active dispersion (such as for example ultrasonic treatment), aggregates can break apart resulting in large fraction of primary particles and small aggregates in the final material.

Another distinctive feature of NDO is the high surface charge in DI water suspensions (and in a variety of other solvents), characterized by the zeta potential. Zeta potential is one of the most important characteristics of the stability of a colloidal system and depends to a large extent upon the type and density of the chemical groups on the nanodiamond surface. This is one of the characteristics where peculiarities of the amount and composition of oxygen-containing groups on the surface of a nanodiamond material play a major role in its properties. Comparative measurements of zeta potentials of fractions of NDO, air purified ND (NDA-415C and NDA-425C), and industrial material RUDDM1 (obtained by soot oxidation by atomic oxygen in NaOH and modified with NaCl)32 were performed. Fractions of nanodiamonds in DI water were obtained by consequent centrifugation: initial polydispersed material was centrifuged at regime #1 (Table 2), fraction 1 was obtained. Supernatant collected and centrifuged at regime #2, and so on. Regimes of centrifugation for NDO and NDA-415C nanodiamonds are shown in Table 2. Two smallest fractions of RUDDM1 were obtained by centrifugation at 25 000g during 10 min. The residue fraction was resuspended in DI water after every centrifugation and sonicated 30 s.

Results of the measurements of zeta potentials are illustrated in Figure 9. Results for the NDS-415C sample are also not shown in Figure 9. As can be seen from Figure 9 suspensions of the fractions of NDO demonstrate much higher zeta potential in absolute values in comparison to the fractions of the initial polydispersed material before centrifugation (approximately −40/−45 mV for all three samples), while zeta potentials of the resuspended residues were significantly increased. An assumption was made that during sedimentation due to centrifugation part of the counterions from the solvation shell around nanodiamond particles was stripped off and left in the supernatant, so that surface charge of the particles in the residue was increased.

To check this assumption, a suspension of ND (5 wt %) in DI water was centrifuged at 25 000g for 10 min. Because of the high concentration of ND, most of the material sedimented. The supernatant was discarded and the residue was collected, resuspended in fresh DI water, and centrifuged again. In this case, zeta potential of the supernatant became lower (higher in absolute value); −60 mV. So indeed, deionization during sedimentation took place; whereas after dispersion of 0.1% NDO in DI water, conductivity of the slurry is approximately 0.03–0.05 mS/cm, after resuspension of a residue in pure DI water (0.1 wt %), conductivity of the slurry becomes approximately 10 times less. The procedure described above was called washing of ND. Experiments with sequential centrifugation (with regimes from Table 2) were repeated for the washed ND for all 3 samples. We did not observe significant difference for the RUDDM1 sample as compared to unwashed sample. For the air-purified ND zeta potentials, the fractions became lower by approximately 5 mV for the washed sample.

The most pronounced effect took place for NDO. For the smallest fractions, zeta potentials of the washed sample were further decreased by 15–20 mV, reaching −100 mV for the smallest processed fraction (Figure 9). This high zeta potential was preserved over a full week (time of observation). After addition of NaOH, the zeta potential rose to −45 mV, similar to the zeta potential for polydispersed material. This again confirms the hypothesis that the origin of high zeta potential is stripping-off of the counterions during centrifugation. For as-prepared (noncentrifuged) NDO, the zeta potential remains constant during titration and does not decrease after addition of NaOH.3 So, even though the three starting materials displayed similar negative zeta potentials for the initial suspensions, the high density of oxygen-containing groups at the surface of NDO caused interesting phenomena during deionization by centrifugation, namely a highly increased surface charge. Because of this high surface charge, some fractions of NDO easily form well pronounced colorful photonic structures.3 It is possible that when the density of counterions around NDO is decreased, hydrolysis of additional anhydride molecules takes place producing carboxyl groups which in turn become charged due to dissociation. This phenomenon warrants further study.

## CONCLUSIONS

Current requirements in methods of nanodiamond purification from detonation soot are centered on achievement of low content of sp2 carbon and small size of agglomerates. Development of inexpensive, environmentally friendly technologies
remains an important goal in the nanodiamond community. Soot purification using ozone treatment satisfies most of these requirements. Nanodiamond of ozone purification possesses several distinct features originating from high density of oxygen-containing groups: very high acidity (pH of 10% hydrosol 1.6—1.8), high oxygen content (more than 13 wt %), enrichment in radical species, low sp² content (absence of sp² carbon in EELS for small NDO fractions), very high z-potential (down to −100 mV), colloidal stability over wide pH range (2—12), high dispersivity of as-received polydispersed powder (160—180 nm in DI water), and a high fraction of small (and primary) particles. On the basis of the TDMS and IR spectroscopy studies, it is concluded that the above properties of NDO originate from surface termination of NDO by carboxylic anhydride groups, covering more than 20—30% of the nanoparticle surface area. It is also hypothesized that the desorption of carboxylic anhydride groups from NDO during heating (TDMS profiles) proceeds by two different mechanisms, possibly due to different binding energies of carboxylic anhydride groups with different crystallographic facets of the nanodiamond particles.

Unexpectedly, zeta potential studies of the NDO fractions demonstrated a very low value for the zeta potential, about −80 to −100 mV, for the smallest fraction obtained by resuspension after centrifugal sedimentation. This phenomenon is possibly caused by removing of the counterions during centrifugation and warrants further studies.

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