Advanced oxidation process for detonation nanodiamond surface chemical modification

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Abstract. An advanced oxidation process has been implemented for detonation nanodiamond surface chemical modification. The treatment intended for chemical oxidation of detonation nanodiamond surface through reactions with ozone in aqueous media. A number of detonation nanodiamond samples were processed: purified industrial grade and single particle hydrosols of air oxidized and hydrogen annealed detonation nanodiamonds. Comparative analysis of surface chemical composition provided by XPS and FTIR data.

1. Introduction
Detonation nanodiamond (DND) is an industrial product obtained by detonation of explosive mixtures with negative oxygen balance[1]. Detonation nanodiamonds have narrow particle size distribution about 4nm and high specific surface. The surface of a diamond nanoparticle is covered with various chemical functional groups which are formed intentionally or during purification procedure. Great efforts are applied to obtain uniform surface chemical structure of DND nanoparticles[2].

Advanced oxidation process (AOP) is a set of chemical treatment procedures designed to remove organic (and sometimes inorganic) species in water by oxidation through reactions with hydroxyl radicals (·OH)[3]. UV-stimulated dissolved ozone decomposition AOP was implemented for DND purification and surface chemical modification. The treatment is intended for removal of all non-diamond carbon through the reactions with hydroxyl radicals (·OH).

The oxidizing or reducing character of any chemical species is given by standard redox potential. Hydroxyl radical has the second highest redox potential, which is lower only than that of fluorine atom[4]. Hydroxyl radical has high capacity to react with DND surface due to high standard redox potential.

Ozone and hydroxyl radicals are known to be used for detonation nanodiamond separation out of detonation carbon[1]. This research is dedicated to AOP treatment of already purified nanodiamonds.
2. Experimental
The handmade apparatus for AOP processing was constructed and a number of samples were treated.

2.1. Setup design
The setup consists of oxygen gas feeder, ozone generation unit with high voltage transformer and UV irradiated reactor. Process gas bubbles through beaker and enriches solution with dissolved ozone. UV irradiation forces ozone decomposition with formation of hydroxyl radicals.

Bottled oxygen of 2 nines purity (GOST 5583-78, technical grade) is blown through ozone generation unit at 0.1 MPa overpressure and 0.2 lpm feed rate.

Ozone generation unit consists of double concentric U-shape glass tubing placed in water filled cylinder. Inner tube is enclosed and filled with an electrolyte. High voltage alternating current is applied to the inner tube and the outer tube is grounded. This forms the barrier discharge in the gap between inner and outer tube. Feed gas is blowing through barrier discharge and oxygen converts to ozone.

Ozone generation unit production rate is 15 g/h and ozone concentration in process gas is about 4.5 wt.%. The production rate and concentration were measured by iodometric wet-chemistry test method according the guideline[5]. Moreover, ozone concentration in process gas was continuously monitored with specialized UV light absorption meter (MELP ИКО-2).

The AOP reactor consists of 500ml glass beaker filled with processed solution, bubbler and UV sterilizer U-shape lamp (254nm). Ozone generation unit was connected with bubbler by PTFE piping. Bubbler is a Schott funnel immersed upside down into the processed solution. The beaker is placed into an ultrasonic bath to intensify the AOP process.

![Figure 1](image1.png)  
**Figure 1.** Scheme of the system. 1 – Oxygen bottle, 2 – flow regulator, 3 – barrier discharge ozone generator, 4 – advanced oxidation reactor, 5 – high voltage AC power supply.

![Figure 2](image2.png)  
**Figure 2.** Advanced oxidation process reactor. 1 – beaker, 2 – ultrasonic bath, 3 – processed solution, 4 – process gas bubbling tube, 5 – UV sanitizing lamp (254nm).
2.2. Processing scheme
A number of samples was treated using advanced oxidation process: industrial nanodiamond (SKTB Tehnolog, Saint-Petersburg, Russia) purified according [6] and single particle hydrosols of air oxidized[7] and hydrogen annealed[8] detonation nanodiamond. Sample designations could be found in table 1.

| Sample                          | Initial | After AOP treatment | Yield (wt.%) |
|---------------------------------|---------|---------------------|--------------|
| Industrial purified DND         | Z0      | Z0_AOx              | <1           |
| Air annealed 430°C, 3h          | Z–      | Z–_AOx              | 15           |
| Hydrogen annealed 600°C, 3h     | Z+      | Z+_AOx              | 15           |

During the processing hydrosols were periodically sampled for FTIR measurements in order to control the surface modification of DND. The processing was carried out until no changes in FTIR spectra were observed. The comparison analysis was performed between initial and completely processed samples.

The initial concentration of detonation nanodiamond hydrosols was about 0.7 wt.%. This value was determined in a series of preliminary experiments as highest possible value of DND hydrosol that have descent transparency for UV lamp radiation. Sufficient UV irradiation is critical for photolysis of aqueous ozone and consequent hydroxyl radical formation [4].

Two step postprocessing was performed for initial and completely processed DND hydrosols. Aggregated nanodiamonds were separated by centrifugation (RCF = 1.8·10⁴ g, 100min) and residue dried at 130°C and weighted (M_R). Small quantity of obtained hydrosols were sampled for DLS and XPS study. Then DND hydrosols were dried in a rotary evaporator (IR–1M2, Russia) at a temperature of 50 ºC and a pressure of 10⁴ Pa. The resulting solid products were additionally dried under vacuum in a desiccator until reaching a constant weight (M_S).

Additionally, small quantity of “Z–_AOx” and “Z+_AOx” dry powders were redispergated in deionized water in ultrasonic bath (35kHz, 100min) for hydrosol stability proof.

2.3. Characterization
The surface chemical structure was characterized by FTIR and XPS. Particle size distributions of detonation nanodiamond hydrosols were characterized by Dynamic Light Scattering. Electrophoretic potentials (ζ-potentials) of DND particles were characterized by Laser Doppler Velocimetry technique.

2.3.1. DRIFT spectra of DND powders. FTIR spectra of dried DND powders were obtained with a SpectraLum FT-08 spectrophotometer equipped with Pike EasyDiff diffuse reflectance accessory. FTIR spectra were collected as an average of 100 scans with a resolution of 4 cm⁻¹. For each measurement 2 mg of DND powder was thorously ground with 200 mg of KBr powder. Baseline correction with asymmetric least squares smoothing and local maximum peak finding were performed for consistent spectra analysis and representation.

2.3.2. XPS spectra of DND films on Si/SiO₂. DND hydrosols were spincoated on a hydrophiliseated Si/SiO₂ substrate to form continuous films. The films were inspected with optical microscope. The XPS analysis was performed on ThermoScientific K-alpha using Al Kα radiation (1486.6 eV). The diameter of the analysed area was 200 μm. Measurements of the samples were made using the Flood Gun option for charge compensation. Obtained spectra were processed and analysed using CasaXPS (version 2.3.12, Casa Software Ltd).
2.3.3. *Particle size distributions of DND hydrosols.* The particle size distribution and \( \zeta \)-potentials of DND particles in hydrosols were obtained by Zetasizer Nano ZS, Malvern Instruments, England.

2.3.4. *Yield estimation.* The yield of centrifugation calculated as \( M_S / (M_S + M_R) \times 100\% \), where \( M_R \) is mass of centrifugation residue and \( M_S \) is mass of dried hydrosol (see section 2.2.). Since the reactor is open there are losses of material with bubbles and microdrops during AOP treatment that prevents precise yield determination. Mass losses could be approximately estimated as 30wt%.

3. Results and discussion

The advanced oxidation processing changes FTIR and XPS spectra of DND samples. AOP treatment of different initial DND samples leads to similar surface chemical structure of the product. The surface of AOP treated DND nanoparticles became covered with oxygen containing functional groups. Particles of AOP treated DND hydrosol have highly negative \( \zeta \)-potential.

Particle size distributions of AOP treated DND hydrosols demonstrate that AOP preserve deaggregated state of DND hydrosols. Introduced nitrate ions \( (NO_3^-) \) cause negligible aggregation, but in general deaggregated DND samples remain deaggregated after the AOP treatment.

Based on DRIFT data the chemical structure of AOP treated samples is similar but the yield of “Z0_AOx” after the centrifugation was negligible. This may also be caused by influence of accumulated nitrate ions or a consequence of particle aggregation mechanism [9].

3.1. *FTIR spectra comparison*

Due to low hydrosol stability the centrifugation procedure was omitted to obtain DRIFT data for “Z0_AOx” sample.

The spectra of “Z–”, “Z–_AOx” and “Z+_AOx” samples are similar except sharp peak 1384 cm\(^{-1}\) (see figure 3). This peak emerges in spectra of AOP treated samples only and can be attributed to absorption of nitrate ion \( (NO_3^-) \) introduced during AOP treatment (see section 3.4). Peak 1270 cm\(^{-1}\) assigned to C–O bending in epoxy functional group [10].

![Figure 3. FTIR spectra of initial and AOP treated DND.](image-url)
Broad peaks 3445 cm\(^{-1}\) and 1628 cm\(^{-1}\) are observed in spectra of all samples. They are attributed to stretching and bending modes of adsorbed water and effectively mask a possible signal of hydroxyl groups that is located in the same spectral region.

A spectrum of “Z+” (hydrogenated DND) contains peaks 2945, 2944 and 2884 cm\(^{-1}\) attributed to signal of C-H\(_x\) groups. AOP treatment leads to elimination of these features. Band 1120 cm\(^{-1}\) can be attributed to either hydroxyl C-O stretching[10] or impurities introduced during chromic anhydride purification. That feature completely vanished from spectra of “Z+_AOx” due to unintentional oxidation chromium to Cr(IV) during AOP process and subsequent washing out.

Peak 1750 cm\(^{-1}\) of “Z0” sample can be attributed to C=O stretching of carboxyl groups[10]. Peak 1796 cm\(^{-1}\) of AOP treated samples either attributed to C=O stretching of anhydride functional groups. AOP treatment leads to gradual position shift of C=O peak from 1750 cm\(^{-1}\) to 1796 cm\(^{-1}\).

Comparative analysis of FTIR spectra reveals that different surface functional groups have been effectively oxidized in advanced oxidation process.

3.2. XPS spectra comparison

The obtained O1s and C1s regions of XPS spectra are presented in figure 4. The strong upshift (up to ~2.7eV) of the spectra of “Z+”, “Z-_AOx” and “Z+_AOx” samples is caused by their electrostatic charging which is the result of low conductivity of these samples and insufficient compensation of such charging by internal flood gun.

The noted spectra contain no discernible spectral features that might correspond to any oxygen containing groups, such as hydroxyl, carbonyl etc. [11]. This fact, which we attribute to the extremely strong charging of these samples makes impossible reliable deconvolution of their C1s and O1s spectra. On the other hand, it does not prevent from their use for standard XPS evaluation of the oxygen-to-carbon ratio (O/C) for which only the values of respective peak areas are required [11].

![Figure 4. O1s and C1s XPS spectra of initial and AOP treated DND samples. After subtraction of Shirley background, the spectra of each DNDs sample were normalized to the area of corresponding C1s spectrum. For the ease of comparison, they are presented in the unified scale of intensity and offset vertically.](image)
Contrary, O1s and C1s spectra of the Z+ sample seem to be undistorted since its C1s spectrum contains evident component (BE ~ 286.5 eV) which may be assigned to the C-OH (hydroxyl) functional group and since the binding energies of O1s peak (BE ~ 531.0 eV) and main C1s peak (BE = 285.0 eV) are in a good agreement with the published data [11].

The O/C ratios evaluated for all studied DND samples are given in Table.2. They confirm in a quantitative way that the advanced oxidation process can provide more than 4-fold increase of O/C ratio in the case of Z+ sample and 25% additional increase of this ratio in the case of already strongly oxidized Z- sample. These facts clearly show that AOP is a very effective technique for obtaining highly oxidized DNDs species regardless of their initial surface chemical composition.

### Table 2. ζ-potential and Oxygen to Carbon ratio.

| Sample   | ζ-potential (mV) | Oxygen to Carbon ratio (%) |
|----------|------------------|---------------------------|
| Z0       | +35±4            | 6.2                       |
| Z–       | -74±2            | 9.2                       |
| Z–_AOx   | -62±4            | 10.9                      |
| Z+       | +82±5            | 2.3                       |
| Z+_AOx   | -50±2            | 9.5                       |

3.3. DLS data analysis

The particle size distribution of initial (a) and AOP treated (b) DND hydrosols are presented in figure 5. Slight aggregation of AOP treated DND hydrosols is observed, but hydrosols are stable. ζ-potentials are given in Table 2. ζ-potentials of DND particles in both AOP treated DND hydrosols are highly negative (–62±4 mV and –50±2 mV), but ζ-potentials of particles in initial “Z–” hydrosol are even more negative (–74±2mV)

Redispersated hydrosols of “Z–_AOx” and “Z+_AOx” samples show values of ζ-potentials and particle size distributions similar to “before drying” ones.

Observed effects could be explained by either accumulation of nitrate ions (NO₃⁻) during AOP treatment or formation of carboxylic anhydride functional groups at DND surface.

![Figure 5](image-url)
3.4. Yield and stability of DND hydrosols.
The centrifugation yield values are 22±2 wt.% for “Z–_AOx”, 20±2 wt.% for “Z+_AOx” and below 1 wt.% for “Z0_AOx”. Estimated values of overall process yields of each sample are given in table 1.
There are byproducts of chemical reactions involved in AOP that gradually accumulates in solution or hydrosol during AOP treatment time. Nitrate ion (NO$_3^-$) is known byproduct of barrier discharge synthesis with nitrogen containing feedgases[12] and bottled oxygen contain small amount of nitrogen. Sodium ion (Na$^+$) is product of leaching of glassware in acid media[13]. Carbonate ion (CO$_3^{2–}$) is product of ozone reaction with dissolved carbon dioxide[4].

These byproducts are electrolytes and have negative impact on hydrosol stability. Consequently yield of advanced oxidation processing may increase in case of absence of these electrolytes. Simple increase of AOP processing time will not lead to increase of the yield.

4. Conclusion
The method for obtaining uniform surface with oxygen-containing functional groups regardless of the source of detonation nanodiamond was demonstrated. The possibility of wet-chemistry oxidative modification of the detonation nanodiamond surface was demonstrated. Advanced oxidation processing could be more convenient for lab scale tasks than conventional gas-phase methods for the surface modification.

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