

# Application-Specific Detonation Nanodiamond Particulate

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## ABSTRACT

Despite a long history of synthesis of detonation nanodiamonds (DND) by commercial producers in different countries, the properties of DND have only recently been significantly improved. The most serious disadvantage of commercially produced DND is their low colloidal stability and difficulties in suspending dry powders completely or partially in liquids. Currently, one of the most important research directions that has allowed the use of DND in advanced nanotechnology applications are DND fractioning and surface modification. These processes strongly depend on the method of DND synthesis and purification by the vendor. When considering a particular application, a process of DND synthesis/purification, fractioning and surface modification are major factors that must be taken into account.

**Keywords:** detonation nanodiamonds, surface chemistry, fractions, nanocomposites, biological applications

## 1 INTRODUCTION

While the current popularity of carbon nanostructures to a large extent is due to interest in fullerenes and nanotubes, a keen world-wide interest has developed over the last few years in the nanostructured diamond materials [1,2] and, particularly, in nanodiamonds of detonation origin invented in 60-s in the former USSR [2]. This class of nanodiamond material is technologically important since detonation nanodiamond can be produced in bulk quantities.

Detonation nanodiamonds are synthesized at the high pressure-high temperature conditions within a shock wave during detonation of carbon-containing explosives with negative oxygen balance. In this method diamond clusters are formed from carbon atoms contained within the explosive molecules themselves, so only the explosive material is used as a precursor material. The explosion takes place in an inert (non-oxidizing) to carbon gas medium that plays the role of a coolant and is either gas (N<sub>2</sub>, CO<sub>2</sub>, Ar, etc.) or ice (water), the so called ‘dry’ or ‘wet’ synthesis, correspondingly. A typical average particle size of DND crystallite is within the size range of 3-5 nm.

The product obtained by detonation, called detonation soot, contains the diamond nanoparticles along with other carbon structures as well as metallic impurities. A variety of techniques can be used to separate the DND phase from soot, for example, by oxidizing the non-diamond carbon. In the final product – DND powder or water suspensions, nano-diamond primary crystallites form tightly and loosely-bond aggregates ranging in the largest dimension from several tens to several hundreds of nanometers. In the powder form micron-sized aggregates are also common.

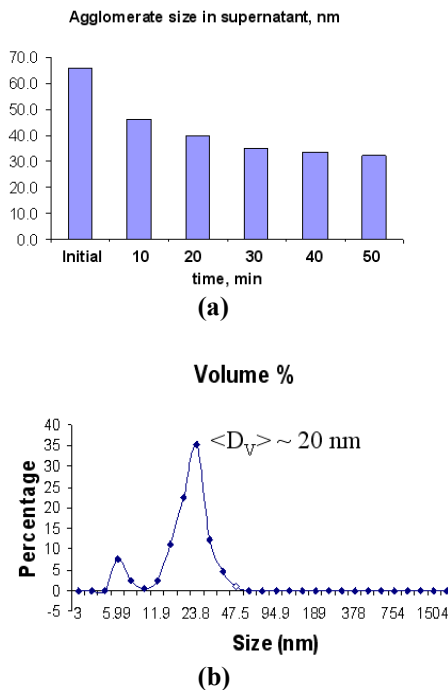
Importantly, new researchers entering the field do not realize initially that there is a wide variety of DND produced by different vendors using different synthesis and purification techniques. The different processes determine the surface chemistry, agglomerate sizes and therefore dispersivity and stability against sedimentation in different types of solvents. While it is possible to isolate the smallest DND particles in the range of ~2-5nm in size in laboratory conditions, agglomeration of the particles remains one of the most serious problems in producing material that is suitable for many nanotechnological applications. We will discuss several approaches to DND modification and surface functionalization that result in particles sizes ranging from tens to hundreds of nanometers that are stable in a variety of solvents. DND specific for biological, polymer composites, and other applications as well as onion-like carbon for electromagnetic shielding produced from DND has been developed and will be discussed. Another important issue in the field of DND is DND fractioning. Starting with as-received polydispersed diamond powder, it is possible to separate it into ~5-7 fractions with a reasonable amount of effort. In addition to resistance to sedimentation that is achieved by changing the surface chemistry, DND fractioning provides particle sizes necessary for particular applications.

## 2 DND PROCESSING

### 2.1 Fractioning

DND fractioning gradually becomes a ‘necessary’ processing step for commercial vendors [3] and can be easily performed in a laboratory using centrifuge and

ultrasound treatment of a suspension. Figure 1 illustrates fractioning of the F1 black fraction of the so called modified ND [4] with average initial particle size 65nm to even smaller size fractions. F1 fraction was initially dispersed in water using a Cole-Parmer® 750-Watt Ultrasonic Homogenizer EW-04711-60, with frequency 20 kHz. Centrifugation was performed using a Cole-Parmer Variable-Speed Microcentrifuge. DND size distribution was measured using a Beckman Coulter N5 Plus particle size analyzer.



**Figure 1.** DND particle size in the supernatant during fractioning of F1 [4] by centrifugation depending on centrifugation time (a). Particle size distribution in the final supernatant. Peaks in the bimodal volumetric size distributions of DND correspond to 6nm (10wt%) and 24nm (90wt%).

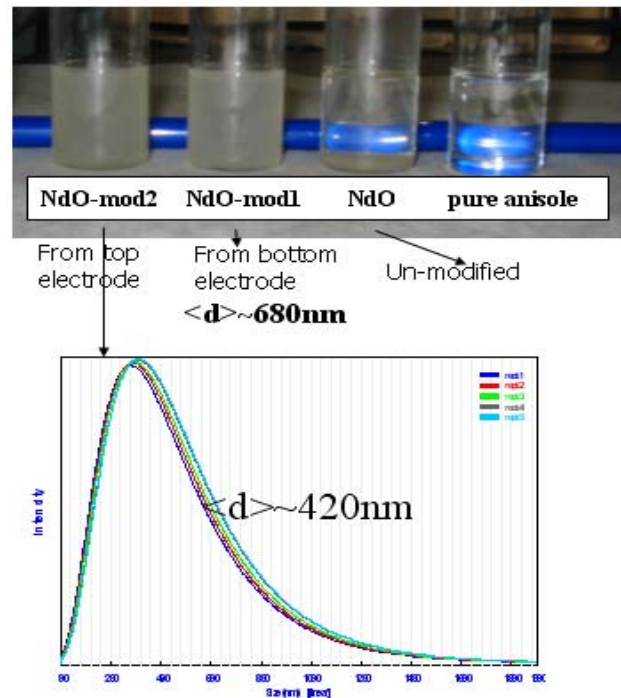
Suspensions with particle sizes about 20nm had been produced.

## 2.2 Surface Modification

There are several methods of changing the surface chemistry of DND reviewed in [1,2]. Recent work at the ITC using a novel atmospheric plasma system (APS) to process and functionalize diamond nanoparticles [5] has been shown to produce a controllable change in the hydrophilic/hydrophobic properties of the particles, which allows them to be dispersed in a variety of organosols (Fig.2). Using wet chemistry methods and a gas flow reactor, fluorination of DND reportedly takes an extended periods of time to complete the surface functionalization (up to several days), while atmospheric plasma-based

processing required just a few minutes. In addition, by using a plasma system that utilizes a discharge that is generated at high pressure, in our case at atmospheric pressure, there are no pumps or valves associated with the chamber that may cause changes in pressure that could disperse the particles accidentally. In the initial studies using this system, the particles were introduced into the plasma chamber using a small box or tray open at the top to allow exposure to the plasma. The first studies were conducted using SF<sub>6</sub> as the active gas. The created fluorine ions react with the nanodiamond surface and forms a stable bond, confirmed by FTIR analysis [5].

The process of fluorination has resulted in the development of polymer nanocomposites with improved thermal and mechanical properties.



**Figure 2.** Illustration of surface functionalization of DND using atmospheric plasma system developed at the International Technology Center, resulting in improved stability against sedimentation for DND dispersed in anisole. Typically as-received from a vendor DND quickly sediments in anisole (third vial from the left) forming agglomerates with sizes of several microns. After treatment in fluorine-containing plasma, DND remains stable in anisole for months (1<sup>st</sup> and 2<sup>d</sup> vials from the left).

## 2.3 IP Related issues on DND

Whenever it is possible, DND producers try to protect the final DND product that bears specific features based upon the method of synthesis/purification [6]. While a 'signature' of DND material has not been finalized, the following characteristics can be considered in order to specify DND produced by different vendors: carbon phase

composition obtained for example, by the x-ray diffraction method; lattice constant; monocrystallite size; specific surface area; elemental composition (in terms of content of incombustible impurities as well as elemental gas-phase composition in terms of C-N-H-O content); the nature and content of the surface groups. Such characteristics as average aggregate size in a specific solvent, zeta-potential in a specific pH-range, possibly FTIR and XRD spectra can be in principle claimed as a 'signature' of the product. However, after decades of study of the properties of DND material, a wide variety of properties had been described as a prior art in the open literature so that probably only a combination of the specific characteristics can distinguish a product sufficiently to be patentable [6].

The elemental composition of DND is one of the important characteristics to be considered in this context [6]. DND elemental composition from different vendors is well characterized and varies according to the literature in the following mass percents: C (75-90%), H (0.6-1.5%), N (0.8-4.5%), O- (4.0-23.6%) [6]. In the full mass balance, it is also important to include content of the incombustible impurities. The prevalence of the elements C, N, O and H in the composition of the surface groups is due to the composition of the explosives used for DND production, a mix of trinitrotoluene and hexogen. Recently it was demonstrated by Spitsyn et al. [7] that this important characteristic can be varied using high-energy hydrogen treatment. The CHN analysis was performed in the C-H-N analyzer of the CARLO ERBA type, model 1107.

**Table 1.** C-H-N composition of the DND Ch-St (purified using acid-chrome anhydride treatment) and Ch-Oz (purification in an ozone-flow reactor). Ch-StH and Ch-OzH are same samples after high-energy hydrogen treatment.

	Ch-St	Ch-StH	Ch-Oz	Ch-OzH
<b>N, wt%</b>	2.38	2.37	2.34	2.41
<b>C, wt%</b>	86.40	89.88	83.78	90.59
<b>H, wt%</b>	0.53	0.67	0.25	0.75

In principle, assuming a spherical structure, a diamond nanoparticle 4.2nm in diameter contains 7193 C atoms total. Out of these carbon atoms 36 are single coordinated, 378 atoms have a coordination of two, and 708 atoms have a coordination of three. The total number of surface atoms, obtained by summing the number of atoms with less than four-fold coordination, is 15.6%. Making an assumption that all carbon atoms should be saturated, for example by H (including surface reconstruction, for example dimer-formation on (001) surfaces), elemental composition of the hydrogenated DND would be C(98.7wt%), H (1.3wt.%). Thus there is, in principle, a reserve for an increase of carbon content in commercial DND.

### 3 APPLICATION SPECIFIC DND

Below we demonstrate for several examples the importance of targeted DND treatment for specific applications.

#### 3.1 DND for Bioapplications

Diamond nanoparticles that are well dispersed and that form highly stable sols in a variety of solvents are critical for the studies of DND biological activity. Besides, DND hydrosols must remain stable after autoclaving. DND suspensions also typically lose their resistance to sedimentation after freezing. Puzur et al. developed modified nanodiamonds [4] possessing all necessary properties mentioned above for bioapplications and performed animal studies of the bio-compatibility and biological activity of modified diamond nanoparticles summarized in [8]. Extended experiments with white mice demonstrated that complete substitution of water by modified diamond nanoparticle hydrosols (0.002-0.05 wt.%) (Fig.3) does not result in the death of the animals, nor does it result in statistically significant weight changes as compared to a control group of animals for the duration of experiments (3-6 months). It was also demonstrated that substituting the hydrosols for water does not influence mouse reproductive ability, at least for the first five generations. Animals consuming the hydrosols from birth reproduced healthy offspring. Blood chemistry, on the other hand, was found to be affected by prolonged substitution of water with diamond nanoparticle hydrosols in both a concentration- and dose-dependent manner [8]. In another series of experiments, intramuscular injections of modified diamond nanoparticles were administered to white laboratory rats (Fig.3). No inflammation of the tissue in the point of injection was found either visually or using cytological methods [8].

These preliminary studies are encouraging for the use of diamond nanoparticles as enterosorbents. The studies clearly demonstrate a general biocompatibility and a distinct dose-dependent bioactivity.

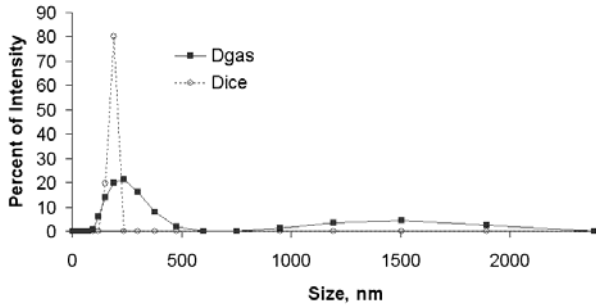


**Figure 3.** Oral (left) and intramuscular (right) administration of modified nanodiamonds to white mouse.

#### 3.2 OLC for EMI Shielding

The annealing of nanodiamonds results in the formation of Onion-Like Carbon (OLC) particles with a structure of concentric carbon shells having various defects in the shell

structures [9]. Type of nanodiamond, mainly type of surface functional groups, which are defined by conditions of synthesis and soot purification, as well as sizes of DND agglomerates influence structure and size of OLC particles and their agglomerates. Preliminary studies demonstrate that the smallest size of OLC in an organosol possesses OLC obtained by annealing of DND produced using ice cooling media during detonation and soot purification in ozone flow reactor (Fig.4).



**Figure 4.** Size distribution of two OLC samples in NMP measured using the photon correlation spectroscopy approach.

Besides, in the studies of electromagnetic (EM) shielding properties of OLC [10], it was revealed that the EM shielding properties depend on the type of OLC (Table 2). In the examples in Table 2, several types of DND obtained from different vendors were used for production of OLC. Some DND were produced in a chamber containing inert to carbon gas atmosphere (Dgas series) and one type of DND was produced using an ice coating around the detonation charge (Dice series). For OLC production, the initial DND were gradually heated up to 1800-2140K temperatures and annealed for several hours in a vacuum chamber (up to  $10^{-5}$  torr).

**Table 2.** Materials, characteristics and EM absorption properties of different types of OLC as well as MWCNT, soot and nanodiamond

	DND annealing T, K	Content of magnetic metal, wt%	Powder Density g/cm <sup>3</sup>	Maximum transmission lost, dB		
				26-37 GHz	8-12 GHz	2-5 GHz
<b>OLC</b>		0.1/Fe				
Dgas1	1800	0.015Cr	0.45	-50	-11	-27.4 (OLC +ND) *
Dgas2	1800	0.15/Cr	0.25	-30	-6	
Dice1	1900	0.15/Fe 0.015Cr	0.2	-21	-8	
Dgas3	2140	0.1/Fe	0.36	-46	-8.8	
<b>MW-CNT</b>	N/A	0.9/Fe 0.4/Co	0.1	-42		
<b>Nano-diamond</b>	N/A	0.3/Cr 0.1/Fe	0.37			-5.6
<b>Soot</b>	N/A	1.3/Fe	0.42			-10.1

\* - Mix of the OLC and nanodiamond. Content of OLC in the mixture is 15wt%.

As can be seen from the table, all nanocarbon powder materials show good EM shielding properties. EM shielding of some types of OLC demonstrated superior properties in the studied frequency ranges as compared to the EM shielding of other types of OLC and MWCNT. Thus the reported results show the high potential of the OLC material to be EM shielding material over a broad frequency ranges. It also demonstrates an importance of a type of DND used for production of OLC.

## CONCLUSION

Several exemplary applications of the DND functionalization/fractioning strategy had been discussed. In order for an end user to be successful in the development of applications of this fascinating material, certification/verification of the product offered by vendors is necessary for the selection of materials suitable for specific applications.

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