

# Detonation nanodiamonds: new aspects in the theory and practice of synthesis, properties and applications

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The review describes the current state of research concerning detonation nanodiamonds, including production, methods of studying the properties and applications. The main achievements in the theory and practice of synthesis of detonation nanodiamonds over the past 15 years are addressed systematically; the influence of control factors on this process, performed using single or mixed explosives, are discussed. A new highly economical and environmentally friendly method for chemical purification of nanodiamonds is described. The operational characteristics of new materials based on nanodiamonds are presented. The application prospects of nanodiamonds in traditional and new fields are demonstrated. The bibliography includes 214 references.

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Translation: Z.P.Svitanko

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### List of abbreviations:

- |  |   |
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| ATR — attenuated total reflection,                                 | OB — oxygen balance,  |
| BAS — biologically active substance,                               | OPBI — highly heat-resistant poly[2,2'-( <i>p</i> -oxydiphenylene)-5,5'-bibenzimidazole], |
| BTF — benzotrifuroxan, benzotris(1,2,5-oxadiazole 1,4,7-trioxide), | PA6 — polyamide 6 (kapron),   |
| CEC — composite electrochemical coatings,                          | PDMS — polydimethylsiloxane,  |
| CNT — carbon nanotubes,  | PPase — pyrophosphatase,  |
| CRZ — chemical reaction zone,                                      | PVA — polyvinyl alcohol,  |
| DB — diamond detonation blend,                                     | RDX — hexogen (cyclotrimethylenetrinitramine),  |
| DGEBA — diglycidyl ether of bisphenol A,                           | TATB — 1,3,5-triamino-2,4,6-trinitrobenzene,  |
| DND — detonation nanodiamond,                                      | TETA — triethylenetetramine,  |
| DP — detonation products,  | TG — a charge of TNT (trotyl) and RDX (hexogen),  |
| DS — drug substance,   | TNT — 2,4,6- trinitrotoluene (trotyl),  |
| FL — fluorescence,   | UHMWPE — ultrahigh molecular weight polyethylene,   |
| HPV — high-pressure vessel,  | UPTFE — ultradispersed polytetrafluorethylene,  |
| NV — nitrogen vacancy,   | VTMOS — vinyltrimethoxysilane.  |

## 1. Introduction

More than 50 years have passed since the discovery of detonation nanodiamonds (DNDs), 4–6 nm carbon particles. The last decade witnessed a revival of the interest in DNDs. The range of raw materials for the synthesis of nanodiamonds is being expanded: new explosives extracted from ammunition are now used. Modified and doped DNDs were obtained, a new environmentally safe and economically feasible processes for their chemical purification appeared. This led to a significant change in the properties of DNDs (for example, high conductivity<sup>1</sup> arising upon doping) and increased the potential for their use in micro- and nanoelectronics. Studying the properties of DNDs and DND-based materials expanded their applications in traditional and new fields.

Not all important DND characteristics correspond to analogous values of large crystallites: the heat conductivity of the DND powder is two orders of magnitude lower than that of a bulk crystal; the radiation resistance of the crystallite can be high only when there are no metal or nonmetal impurities on the surface or in the pores of the DND powder; chemical inertness of the DND core is only implied, since the functional groups present on the nanocrystal surface make it, conversely, fairly chemically reactive. Doping of DND crystallites with heteroatoms (nitrogen, silicon, phosphorus, boron) results in the change in optical, magnetic and thermophysical properties. Currently, nitrogen doping of DND crystallites to give nitrogen vacancy (NV) centres is considered to be most promising. These nanocrystals can be regarded as elements of a quantum computer. The generation of NV centres in DND crystallites can give an impetus for the development of nanodiamond spintronics.

The studies of properties of pristine and modified DNDs are being expanded, and the number of relevant publications increases every year.<sup>2–4</sup> The interest is evidently focused on practical application of DNDs in various fields of science, technology, medicine and biology.

Detonation nanodiamonds can serve as examples of diversity and inexhaustibility of the properties of the nanoworld. They belong to the family of nanocarbons, which includes fullerenes, carbon nanotubes, graphene, globular nanocarbon, onions and other structures, and are among the few products that are commercially manufactured. Traditionally, DNDs are produced in industry starting from mixtures of 2,4,6-trinitrotoluene (TNT) and RDX (cyclotrimethylenetrinitramine) in which the component ratio is 50:50 or 60:40. Other aromatic nitro derivatives, for example, tetryl (*N*-methyl-*N*-2,4,6-tetranitroaniline), have also been proposed for this purpose. The DND production at the Plant of Plastics (Kopeisk, Russia) is wholly based on the use of tetryl.

The originality of the method of DND synthesis consists in the fact that the ‘surplus’ carbon atoms in the molecules of explosives serve as the source of carbon, that is, the starting compounds have a negative oxygen balance (OB).<sup>†</sup> In other words, they contain less oxygen than it is necessary for oxidation of all combustible components. The use of

DNDs in various industry branches is driven by the need to crucially improve the performance characteristics of composite materials. With the existing level of development of the synthesis and understanding of application prospects of DNDs, they are now considered among the most advantageous carbon nanomaterials for nanotechnologies.

The purpose of the present review is to systematize the available data on DNDs, taking into account their unique properties, new production processes and applications in various fields of science and technology. This is not an exhaustive description, in view of the limited size of the review, but an account specially addressing the above aspects.

## 2. Detonation synthesis of nanodiamonds

### 2.1. Possible mechanism of the synthesis of nanodiamonds

The views on the mechanism of the detonation synthesis of DNDs that prevailed a decade ago are described in detail.<sup>5–7</sup> This description is fragmentary and often contradictory. In view of the enormous temperature (3000–4300 K) and pressure (20–30 GPa), thousands of chemical reactions involved, and, what is most important, short time of the detonation transformation of explosives (0.1–0.3 μs), currently there is no evidence-based proof for the processes that take place in the space from the detonation wave front to the Chapman–Jouguet plane,<sup>‡</sup> *i.e.*, in the chemical reaction zone<sup>§</sup> (CRZ). Therefore, it is also difficult to conceive the chemical and physical processes that originate upon expansion of the gaseous detonation products (DP)<sup>¶</sup> and involve condensed carbon. It is believed that at least 80% of the explosion energy is released in the CRZ, while correspondingly ~20% of the energy is released behind the Chapman–Jouguet plane.

In many studies (*e.g.*, Refs 8–12), it is assumed that the major process of formation of DND crystallites starts after the detonation wave front has propagated up to the Chapman–Jouguet plane and ends much further from this plane upon DP expansion. The growth of DNDs is terminated not only because of decrease in the pressure and temperature, but rather due to decrease in the concentration of carbon radicals.

Meanwhile, there are different points of view on the DND formation process. The use of small-angle X-ray scattering made it possible<sup>13,14</sup> to study the evolution of carbon particle size since the appearance of explosive detonation front. Immediately behind the detonation front, the authors detected condensed carbon nanoparticles with a density exceeding the density of plasma in the CRZ and determined the size of these particles to be up to 2 nm. As the process goes on, the diameter of dense nanocarbon particles (*d*) increases to reach, within ~4.5 μs, different values depending on the type of initial explosive. For explosives such as 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), a mixture of TNT and RDX (TG), and benzotriuroxan (BTF), the *d* values were as follows

<sup>‡</sup> Plane in which the energy release stops and the substance flux velocity is equal to the local sound velocity.

<sup>§</sup> Chemical reaction zone is the area located immediately behind the detonation front of the explosive (hundreds of micrometres) separating the initial explosives from gaseous explosion products. In this zone, heat evolution takes place, its temperature is ~3000–4500 K, the pressure is ~18–35 GPa and the substance density is ~2.3 g cm<sup>-3</sup>.

<sup>¶</sup> Gaseous and solid products formed upon detonation of the explosive.

<sup>†</sup> Oxygen balance is the mass of oxygen that remains after oxidation of all carbon contained in explosive molecule to give carbon dioxide and oxidation of all hydrogen to give water divided by the mass of the taken explosive, expressed in percent. Nitrogen is assumed to remain in the free state.