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RESEARCH ARTICLE

Chemical-Biological Activity of Nanodiamond Colloids

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Abstract

The study of the Nanoscale Diamonds (NDs) and their water suspensions has opened huge opportunities for their technological and biomedical applications. Therefore, the interaction of ND with water is actively studied. However, insufficient attention has been paid to the biochemical behavior of suspensions with low carbon content, despite their great scientific prospects. This work aims to fill this gap in scientific literature.

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Introduction

The nanoscale diamond is intensely studied for its biochemical and biomedical applications [1-5]. Since ND is often used in the form of concentrated aqueous suspensions, many patents, scientific studies and reviews are devoted to this topic, but insufficient attention is paid to the study of the physico-chemical and biological properties of dilute colloidal solutions (henceforth called 'Diamond Water', DW), which show unique properties of great scientific significance. The present work describes chemical and biological behavior of ND particles in DW.

The ND used in this work, with typical crystal (primary particle) sizes of 4-5 nm, was produced in our laboratory by detonating a 1:1 blend of TNT and RDX enclosed in an ice shell, designed for fast quenching of the detonation products and thus preventing the annealing of diamond into graphite by the residual heat of the explosion. Explosive experiments were carried out in a vacuumated chamber. The detonation soot was then subjected to intense oxidation to remove the graphite component and isolate the ND powder [6].

Aqueous ND suspensions with high carbon contents (up to 3.1 [7], 8.6 [8], 10 [9], 50 [10] wt%) have been reported; these are colored (even if transparent) liquids or non-transparent slurries. On the contrary, DWs containing only ca. 0.01-0.1 wt% of ND [6 -11], are colorless liquids, apparently clear (to naked eye). We prepared DW by dispersing (by stirring and sonication) 1 % of ND in high-purity water, intense centrifugation of the mixture and removal of the solid precipitate. DLS studies showed the

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particle sizes in DW to vary from tens to hundreds of nanometers [11,12], indicating a very strong tendency of primary ND particles to agglomerate. However, colloids of mono-dispersed ND (i.e. separated primary particles) are also known, particularly used (with grafted Gd or Mn atoms) as MRI contrast reagents [13-15].

Results

Biological nature of 'diamond-water fibers' (DWF)

In vials of DW exposed to atmospheric air at room temperature, after periods of time ranging from several days to weeks, cloudy and then cotton Wool-like Fibers (DWF) emerged and gradually increased in size. Evolution of DWF shapes and sizes in DW begins with globular features ca. a few µm in diameter, which then coagulated into larger quasi-spherical clusters of the order of 100 µm. A microscopic study showed that these agglomerates contain entangled light-brown or grey fibers, on the order of 1-2 µm thick and up to 1 mm in length, emerged and ultimately grew to several mm, sometimes up to 1 cm long. Earlier, biochemical (staining) tests proved the biological nature of DWF [16,17].

In the present work, we studied the DWFs with optical (Figure 1) and scanning electron microscopy (Figure 2) and found them to consist of mycelial hyphae, fungal spores and bacterial cells (thin bacilli- and cocci-like structures) with the diameters in the usual ranges of 1.5 to 18.0 µm, for hyphae, 2.5 to 4.5 µm for spores, and 0.25 to 0.75 µm for cocci, while the bacilli had width of 1 to 2 µm and length 2 to 4 µm. The hyphae were attached to, and apparently 'irradiated' from, agglomerates of ND particles (Figure 1). The fungi formed conidiophores with individual spores. The spores and bacteria were both entangled on the surface of the fungal mycelia and free-floating in solution.

The mycelia of the following fungal species were identified: *P. cyclopium*, *P. aurantiogriseum*, *P. aurantiogriseum*, *P. chrysogenum*, *P. lilacinum*, *B. bassiana*, as well as some species of the genera Mucor, Rhizopus, Trichoderma and Aspergillus. Some species distinguished by dark-colored mycelium with chlamidospores, or light-colored mycelium, as well as several types of bacterial mucous colonies (white, rosy and light yellow) and colonies characteristic of *B. mycoides* were observed, without full identification.

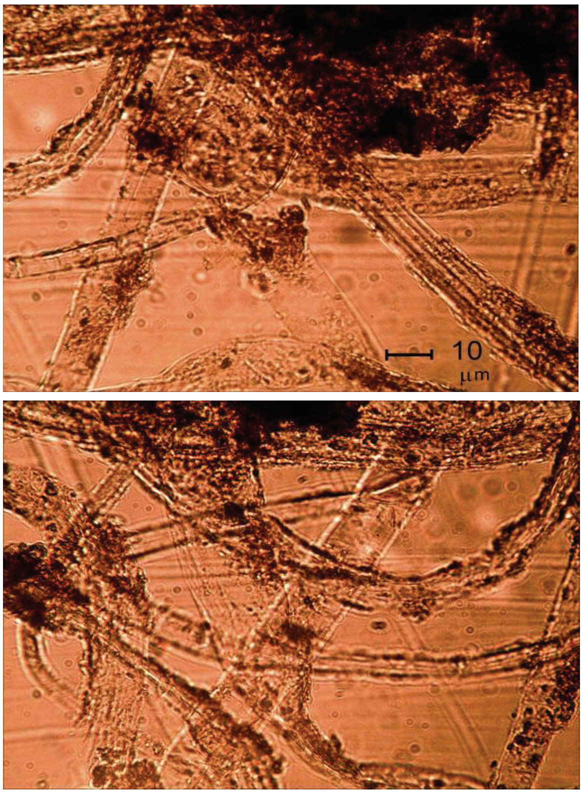

Figure 1 DWF photographed in immersion oil with n = 1.60, using optical microscope with 600-fold magnification.

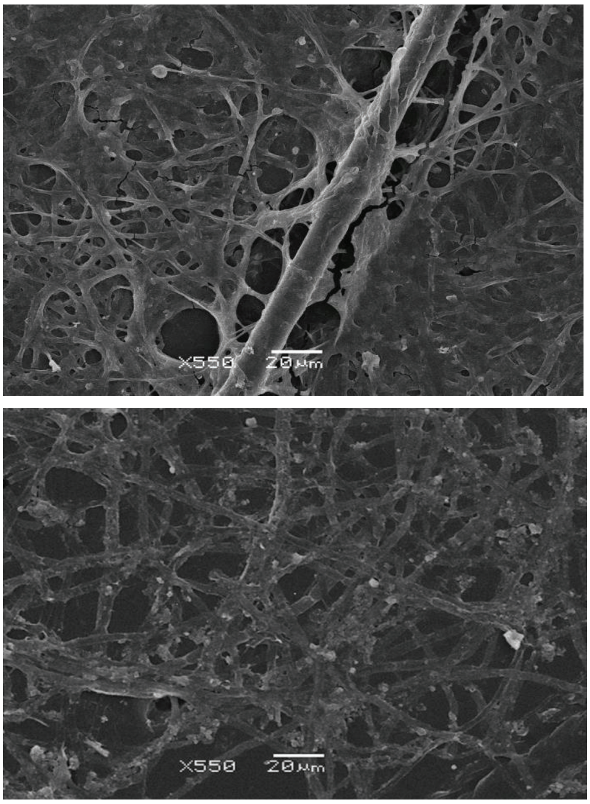

Figure 2 Scanning electron microscopy of fungal hyphae and spores in DWF.

Table 1: Composition of WDFs, depending on their age.

Sample	Age,	Elemental analysis, wt%				C/N ratio
No.	months	C	N	H	O	
1	0*	86.5	2.15	0.5	*ca.* 10	40.2
2	1	69.6	4.2	1.2	25.0	17.2
3	2	49.0	4.4	1.7	44.5	11.2
4	3	15.7	14.9	3.0	66.4	1.05
5	4	2.65	17.8	5.3	74.25	0.15

Inoculation with the original ND powder did not produce the growth and formation of colonies of fungi or bacteria for 10 days, although individual bacterial cells and fragments of mycelia were detected. Inoculation with original ND exposed to air and moisture for a short time, already after 1 week yielded isolated colonies of *P. bacteria*, particularly *P. cyclopium*, clear white mycelium, and *B. mycoides*; on the third week, fungal colonies evolved, distinguished by clear dark-coloured mycelium.

Neither fungi nor bacteria were isolated using ND previously sterilized in an autoclave (at 1 atm and 120°C), whether immediately before the tests or after kept hermetically sealed for 1 year. Even after a protracted (1 month) incubation of sterile ND in sterile water, fungi or bacteria did not emerge or grow. If the original ND was placed into sterile distilled water, 1 month later some isolated fungal hyphae and bacterial cells were detected. If a sterile ND powder was incubated in ordinary distilled water or a distilled water previously exposed (for 1 to 3 h) to atmospheric air, then the growth of fungal mycelia and bacterial cells was also observed. Note that in blank experiments – identical vials of pure water kept alongside the DW vials no fibers were formed; moreover, if transplanted there, the already formed DWF failed to grow and soon died.

Chemical composition and evolution of DW and DWF

For elemental analysis, samples of DW with DWF of different ages were dried at 150°C and analyzed using Carlo Erba 1106 instrument (standard errors of 0.3, 0.1, 0.05% for C, H, N, respectively, each sample analysed twice). The balance can be attributed entirely to oxygen, for although the original ND contained small amounts of Fe (≤ 0.2%) and Si (≤ 0.3%) extracted by shock waves from the steel walls of the explosion chamber and yielding non-combustible residue, these heavier impurities were practically removed by intense centrifugation of DW.

The results (Table 1) show a steady decline of the carbon content over time, while those of all other elements increase. During the growth of DWF (first two months) the C/N ratio was intermediate between those of the initial ND (40) and living organisms (5 to 10 for fungi and bacteria), as could be expected for the mixture of these. IR spectra of the DWF at this stage [16] show the stretching bands C-O at 1026 and 1154 cm^{-1} of carbohydrates; C = O 1746, CH2 or CH3 2853 (symm) and 2934 cm^{-1} (asymm) of lipids; C-N 1420 cm^{-1} of proteins, as well as amide bands of the latter at 1638, 1548 and 1316 cm^{-1}, all typical for living micro-organisms, especially fungi [18]. Later, the lysis of the micro-organisms sets in, releasing carbon as CO2 (which escapes, hence the dwindling carbon content) and nitrogen as NH4^{+} or NO3^{-} (which stay in solution). The high oxygen content, ultimately reaching 74.25%, is somewhat unusual, although NH4NO3 (which was in fact isolated, see below) contains 60%.

Actually, the atomic composition of samples 2 to 5 in table 1 can be rationalized respectively as:

$\mathrm{C5.8\ N0.3\ H1.2\ O1.55 \rightarrow 28C{\cdot}5CO{\cdot}2H2O{\cdot}NH4NO3}$

$\mathrm{C4.1\ N0.3\ H1.7\ O2.78 \rightarrow 19C{\cdot}3H2O{\cdot}5CO2{\cdot}NH4NO3}$

$\mathrm{C1.3\ N1.05\ H3\ O4.15 \rightarrow CO{\cdot}H2O{\cdot}CO2{\cdot}NH4NO3}$

$\mathrm{C0.2\ N1.25\ H5.3\ O4.65 \rightarrow 2H2O2{\cdot}NH4NO3}$

Admittedly, the presence of O-O bonds may seem far-fetched, but the products was indeed unstable and exploded under 23-25 k bar of static compression and under heating in argon at T > 200°C [19].

A faster evolution of the chemical composition was observed with DW prepared by bead-milling procedure. 6.5 g of ND and 50 ml of water were placed in a planetary bead mill with both the 80 ml pot and the 25 beads of 5 mm diameter made of WC-6 alloy (tungsten carbide doped with 6% of Co), which was rotated at 650 rpm for 30 min in either direction, After the milling, 10 ml of the liquid phase was placed in an open vial to dry at room temperature. The dry residue had the composition: C 42.55, H 3.02, N 3.36, O 51.07%. Repeated experiments have shown that during very slow evaporation of DW (from a vial with a pinhole in the lid), powders of white, yellow and reddish colors were consequently precipitated, with the compositions (%):

(i) Colorless C 15.35, H 7.15, N 10.15, O (balance) 67.35

(ii) Yellow C 13.3, H 3.89, N 9.02, O (balance) 73.79

(iii) Reddish C 0.58, H 3.95, N 19.88, O (balance) 75.59

Recrystallization of the entire sediment from DW after prolonged (several weeks) evaporation, yielded a solid with the composition C 0.98; H 4.64, N 26.70, O (balance) 67.68%. Remarkably, the compositions of the latter phase and the reddish solid correspond to $NH4NO3 \cdot ⅓\ H2O$ and $NH4NO3 \cdot H2O2 \cdot O2$, respectively. Since these formulae are close to the ammonium nitrate, we have extended the exposure of DW (40 ml) to air to 18 months, whereupon the liquid colloid converted into a solid mixture of powder (2.1 g) and colorless crystals (19.4 g) with content (%):

	C	H	N	O	Formula
Powder	1.90	4.80	33.64	59.66	$NH4NO3 \cdot C0.13$
Crystals	0.22	5.10	33.75	60.93	$NH4NO3$

Interestingly, the carbon content in these solids (0.08 g) was close to that in the original DW (0.2% in 40 ml), indicating that ND participated in the formation of NH4NO3 as a catalyst. Results of the X-ray study of all above-mentioned samples are presented in figure 3.

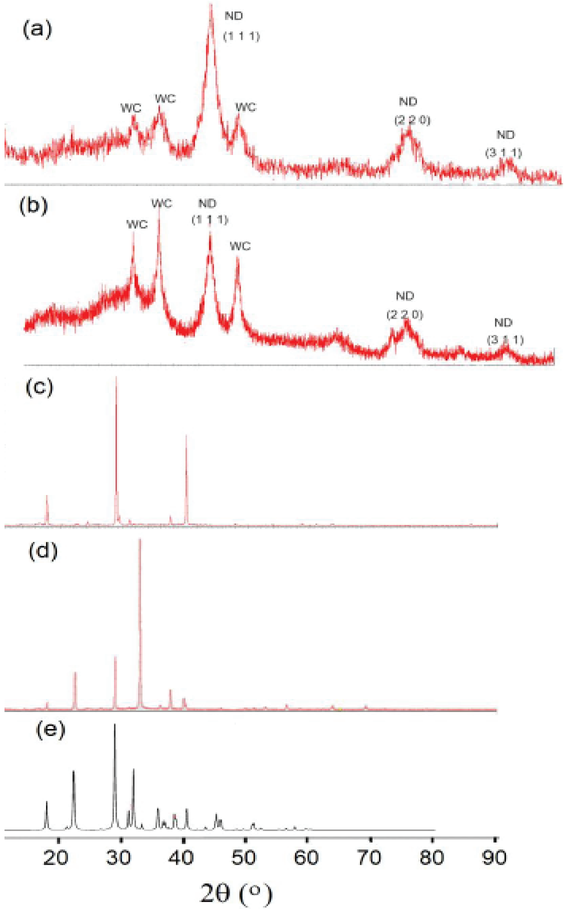

Figure 3 XRD patterns (Cu-*K*α radiation, λ = 1.5406 Å): (a) DND bead-milled in water, (b) white sediment formed in the latter after 1 month, (c) reddish crystalline sediment formed after 4 months, (d) after 18 months, (e) phase IV of NH_4NO_3, simulated from single-crystal data. In (a) and (b), reflections of ND and WC are labeled.

Discussion

As shown above, DWFs are colonies of fungi and bacteria growing around ND particles. Obviously, bacterial and fungal spores are omnipresent in atmospheric air and infestation of water exposed to it is only a matter of time. However, we found that an admixture of ND, even in small concentration, greatly facilitates such infestation and subsequent growth of bacterial and fungal colonies, while no such colonization occurs under the same conditions in pure water – where the spores can get with equal probability.

The effects of ND on living cells have been studied extensively, but usually with the focus on biocompatibility, i.e. the absence of cytotoxicity. The possibility of ND encouraging cellular (including bacterial and fungal) growth has not attracted the attention it deserves, given the practical applications of ND in medicine (drug delivery, biocensors, etc.).

Is it possible that ND can supply the micro-organisms with some vital nutrients? ND particles have a unique chemical activity due to their small sizes. This ‘size effect’ is caused by increasing fraction of surface atoms with lower coordination numbers, e.g. by increasing number of dangling chemical bonds in fine powders [20], which results in reducing surface tension, melting point, heat capacity and cohesive energy in nanophases [21-23]. Experimental data and all theoretical models show that the cohesive energy of nanoparticles falls linearly with their sizes.

According to [24] the cohesive (atomization) energy of a particle (Ep) of arbitrary size is related to that of the bulk solid (Eb) as

$$Ep = (Np/Nb)\ Eb \qquad (1)$$

Where Np is the average coordination number of atoms in the structure of particle and Nb is that in the bulk. Since Np < Nb, the atomization energy of particles will decrease, thus enhancing their reactivity. Calculations of Ep by Eq. (1) for Cu, Au, C, Si, Ge, Mn, Fe, Co, Ni, and Pt using atomization energies in bulk (Eb) and 5 nm-sized (Ep) elemental elements show that the average relation Ep/Eb = 13 ± 1% [23]. We also found experimentally [23] that Group 4 elements in nano-state, due to their increased reactivity, change their positions in the electrochemical sequence and replace hydrogen in water under ambient conditions (E = C, Si and Ge):

$$E + 2H2O = EO2 + 2H2 \qquad (2)$$

The natural conversion of N2 to NH3 is mostly realized by nitrogenases in bacteria, where the MoFe-protein or the Fe-protein work in tandem for the activation or reduction of N2 molecules, respectively [25]. This reaction has been realized by contact glow discharge under a voltage of 500-600 V in an aqueous solution, where N2 serves as both the electron donor and acceptor.

Alternatively, we can consider the use of ND to realize the direct reactions

$$2C + N2 = C2N2 \qquad (4)$$

$$C2N2 + 2H2O + ½O2 = NH4NO3 + 2C \qquad (5)$$

Where C is nanocarbon in DW, and N2 is atmospheric nitrogen; the composition of sample 5 in table 1 is consistent with a combination of reactions (4) and (5). Under standard conditions, Eq. (4) is endothermic (ΔH = 309 kJ/mol) and requires heating to > 1400°C to proceed. However, this refers to bulk diamond with the atomization energy Ea = 716.7 kJ/mol; but this reaction would be exothermic for atomic carbon with ΔH = – 1124.5 kJ/mol or with ΔH = – 506.5 kJ/mol for C2 molecule. DSC experiments on ND powders showed the heat of combustion ΔHc (ND) = 37.7 kJ/g (or 43.3 kJ/g for the carbon content only), ca. 30% higher than for polycrystalline diamond, 33.0 kJ/g. Thus, reactions (4) and (5) for ND will proceed exothermically. Note that ND in reactions (4) and (5) acts as a catalyst for the formation of NH4NO3; catalytic properties of ND and WC in other reactions were reported earlier [26-28]. This explains why the process was facilitated if a colloid was prepared using bead-milling procedure (see above).

Thus, an interaction of ND particles with atmospheric nitrogen in water medium forms ammonium nitrate, e.g. a fixation of atmospheric nitrogen occurs. It is very important since nitrogen is an essential element for all living organisms. The importance of atmospheric nitrogen fixation, which has been carried out by the Haber-Bosch method for more than 100 years, is evident from the huge scale of global ammonia production (170 million tons per year), which accounts for up to 1-2% of the total global energy consumption. The high cost, high energy costs and environmental harm (the release of a huge amount of carbon dioxide into the atmosphere) in this method make us look for alternatives, to which up to 30,000 publications and citations for the topic of ammonia synthesis have been devoted annually [29].

An amazing feature of this process is the formation of the final product in the form of large crystalline grains of NH4NO3 (see the photograph in [30] as a result of a very long (1.5 years!) contact of ND particles in colloidal solution with air. A very small concentration of these particles, which served as centers of crystallization of the formed NH4NO3, remained in the form of 0.2% carbon in the composition of NH4NO3 crystals, as shown by chemical analysis. The slow kinetics of these reactions is explained by the same low concentration of ND, which is a carrier of fixed nitrogen from air to water.

Conclusion

Bacteria and fungi can flourish in highly dilute colloidal solutions of ND in the manner not observed in pure water. Their growth is facilitated by fixation of atmospheric molecular nitrogen on ND particles (which provides the microorganisms with a vital nutrient), made possible by high reactivity of ND which makes the reaction of carbon with N2 an exothermic process. The resulting enrichment of the media with bioaccessible nitrogen is also confirmed by formation of NH4NO3 crystals after long exposure to air.

Competing Interests

The authors declare no competing interests.

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