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Surface Characterization of Detonation Nanodiamond Particles

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Abstract—Specific features of formation of stable suspensions of detonation nanodiamond (DND) in media of different polarities were considered. A relation between the dispersity of DND particles and their surface activity was found. The surface activity of diamond nanoparticles (10–100 nm) is significantly (by a factor of 4) lower than that of submicron-sized particles, which indicates satisfactory environmental parameters of nanosized diamonds. An attempt to reduce the surface energy by grafting hydrophobic radicals led to appreciable increase in the dispersity of DND particles, thereby reducing the risk of harmful DND effect on the environment.

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Addiction and enhanced resistance of pathogenic microorganisms and viruses to latest antibiotics become a challenging issue to human health protection. Therefore, development of methodology for the design of biologically active agents with an acceptable cost, which do not induce addiction, is undoubtedly of great scientific and practical interest. Efforts of many research groups are aimed at using nanosized particles to solve this problem. A strong biological effect of some metal oxides on Gram-positive and Gram-negative bacteria was shown. Extensive studies are performed on highly active nanosized metal particles. For example, the ability of gold nanoparticles to interact with living cells and penetrate thereinto stimulated studies on grafting of various biological macromolecules (proteins, amino acid) to the surface of gold nanoparticles with a view to deliver drugs directly to affected tissue. In recent time increasing attention is given to prospects in medicinal and biologal applications of detonation nanodiamonds (DND).[1]

Detonation nanodiamond powder may be regarded as nanostructured matter. The procedure for isolation of DNDs from amorphous detonation products includes treatment of their surface with strong oxidants. As a result, some functional groups having a labile proton appear on the surface thus making it hydrophilic. High dispersity and the presence of functional groups are the two main parameters that underlie almost all attempts to put DNDs into practice. At present, DNDs are used most efficiently in medicine and biology [1]. As a rule, potentially high adsorption capacity of DND particles is exploited, for it ensures formation of complexes with physiologically active molecules and their delivery to target organ (drug delivery). It should be noted that the stage of preparation of high-disperse DND suspensions in both polar and nonpolar media is crucial for many practical uses. Here, the main issue is that highly dispersed particles strongly tend to aggregate; therefore, it is impossible to obtain a stable suspension without additional treatment. As a rule, stable DND suspensions are prepared under conditions of ultrasonic treatment and/or via modification of DND surface with surfactants.

The minimal size of DND particles is 4–6 nm. In a real case, submicron range is typical of DND particles, especially in dry powder. Ultrasonic treatment (ultrasonication) of DND suspension is aimed at converting the maximal possible amount of DND to the nanosize range. It should be noted that the adsorption capacity of particles is closely related to their surface energy. According to model calculations,

[1] Detonation nanodiamonds constitute the crystalline fraction of products formed by detonation of mixed explosives under low oxygen.

Surface energies of low- and high-dispersed DND particles

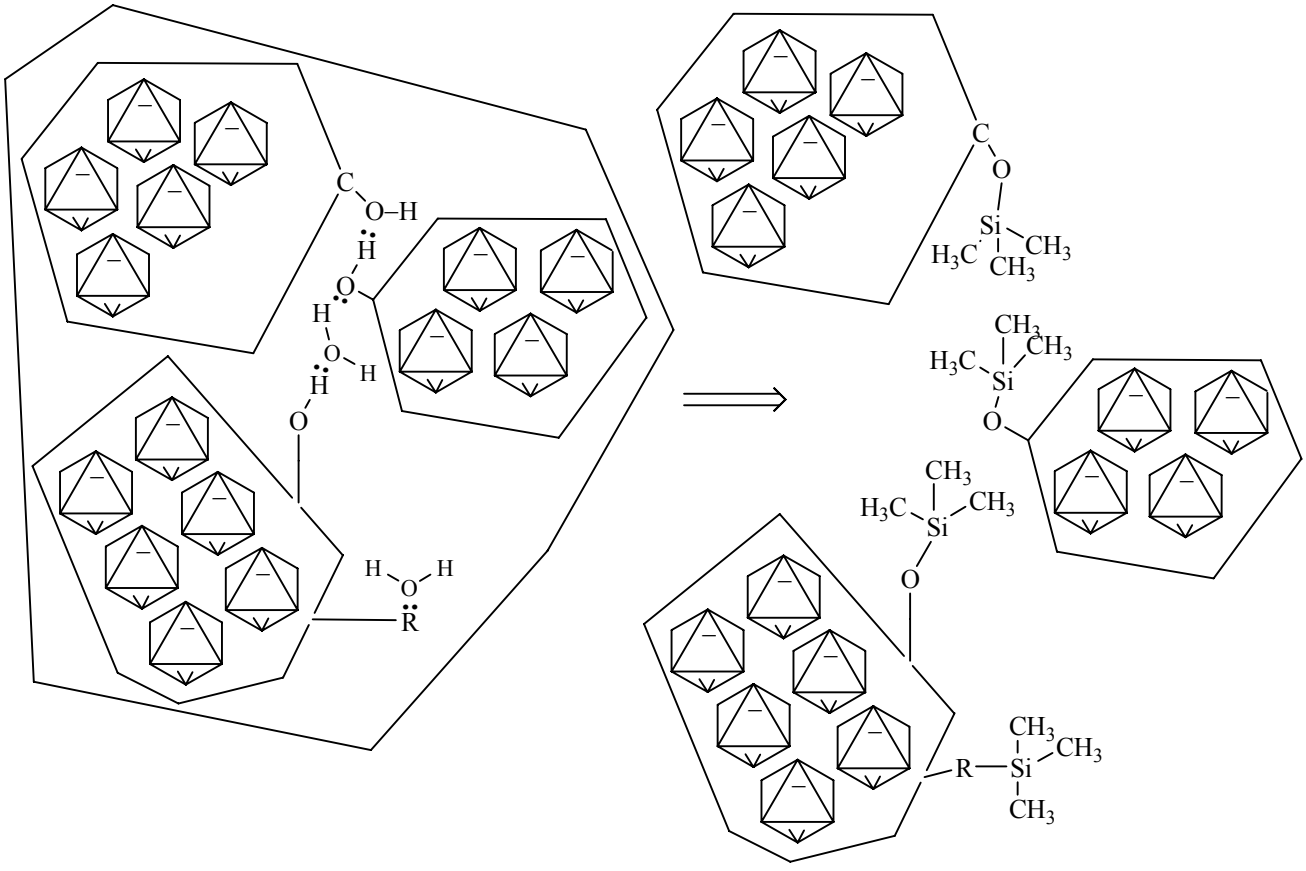
Temperature, °C	γ_L, mN/m	
	DNA-1	DNA-2
50.0	40.8	9.9
55.0	44.3	10.1
60.0	44.0	10.9

the surface energy decreases as the particle size approaches the nano range [2].

In the present work we performed calculations with a view to elucidate a relation between the surface energy of DNDs and their dispersity.

Fractions of DNDs of different dispersities were obtained by ultrasonication of a DND suspension in water to achieve maximal concentration of nanosized DND particles. The optimal ultrasonication time was determined by special experiment and was 5 min. After ultrasonic treatment, the suspension was allowed to settle down over a period of 20 min, and the lower part was separated by decanting. We thus isolated arbitrarily low- and high-dispersed DND fractions, DND-1 and DND-2, respectively.

By dynamic light scattering we found that DND-1 contains particles with a size of 200–600 nm. The particle size in DND-2 ranges from 10 to 100 nm. The surface energies of DND particles were determined from the data of reversed-phase gas chromatography [3]. Taking into account the equality of the contribution of dispersive (London) forces to the work of adhesion (W_A) and the Gibbs energy variation for desorption of a methylene group from a unit area, we arrive at



Chemical modification of DND particles; R is a functional group containing an active proton (OH, NH_2, COOH, etc.).

$$W = \Delta G[A(CH_2)] / N_{AV} a(CH_2), \quad (1)$$

where N_{AV} is the Avogadro number, and $a(CH_2)$ is the area occupied by methylene group on the adsorbent surface. The Gibbs energy per mole of methylene groups can be calculated by the equation

$$\Delta \bar{G}[A(CH_2)] = -RT \ln (V_R^{n+1}/V^n), \quad (2)$$

where R is the universal gas constant, T is the temperature, and V_R^{n+1} and V^n are the retention volumes for normal alkanes having $(n+1)$ and n carbon atoms, respectively. When normal alkanes are used as sorbate, only nonpolar forces contribute to $\Delta G^0[A(CH_2)]$; consequently, this quantity corresponds to the work of adhesion between a nonpolar liquid and solid surface.

The work of adhesion is given by the known Fowkes equation:

$$W_A = 2(\gamma_1 * \gamma_2^L)^{1/2}, \quad (3)$$

where γ_1 is the surface tension of nonpolar liquid, and γ_2^L is the dispersive (London) contribution to the surface tension of the second component. Combination of Eqs. (2) and (3) gives Eq. (4) for the calculation of γ_2^L:

$$\Delta \bar{G}[A(CH_2)]/Na(CH_2) = 2[\gamma^*(CH_2)\gamma^L]^{1/2}. \quad (4)$$

The results are collected in Table 1. In fact, it is seen that increase in the dispersity leads to reduction of the surface energy.

Dispersion of DND particles in nonpolar medium requires preliminary chemical modification of their surface. An efficient method for blocking proton-active functional groups on a solid surface is based on the silylation reaction. The silylation was performed using equimolar mixtures of Me_3SiCl with $(Me_3Si)_2NH$ and of $Me_2ViSiCl$ with $(Me_3Si)_2NH$ (Me = CH_3; Vi = CH_2=CH).

We anticipated that the surface character will be determined by grafted trimethylsilyl groups, i.e. it will become hydrophobic with simultaneous elimination of adsorbed water and hydroxy functional groups. However, the result of the above modification was surprising and difficultly predictable, namely the degree of dispersity of DND in polar medium increased (the number average diameter of DND particles decreased from 23 to 15 nm). Attempts to rationalize the observed pattern led us to a model of DND cluster stabilized by hydrogen bonds formed between different functional groups (see figure) on the particle surface, as well as by water molecules like those present in zeolite. Silylation induces cleavage of stabilizing bonds, thus generating a new surface.

The fractal model of DND aggregates implies theoretical possibility for their decomposition into N initial particles. However, due to steric hindrances intrinsic to the silylation reaction, decomposition of only loosest aggregates is possible, and the system is stabilized again.

It was also interesting to trace how the DND preparation procedure affects the concentration of surface labile proton-containing groups. For this puprose, the Chugaev–Tserevitinov technique was applied. The results showed that, despite attempted surface hydrophobization, the number of surface hydroxy groups even slightly increased (from 2.78 to 2.94). This indicated emergence of latent groups on the newly formed surface. Thus the model for stabilization of DND clusters by hydrogen bonds is validated.

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