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Environmental Issues Related to Preparation of Detonation Nanodiamonds. Surface and Functionalization

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Abstract—Specific features of the preparation of detonation nanodiamond (DND) surface were considered from the viewpoint of their subsequent use in biology and medicine. Particular attention was given to quantitative determination of groups containing a labile proton on the DND particle surface. It was proposed to use only physical drying techniques to improve environmental parameters of DND surface functionalization techniques. The proposed procedure ensured for the first time additional purification of DND from latent carbon, which considerably improved their environmental properties.

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The procedure for the synthesis of ultradispersed diamond particles by controlled detonation of explosives has been considerably improved in the past decades [1]. In modern literature, this type of diamond is called detonation nanodiamond (DND). The synthetic technology turned out to be so successful that it ensured preparation of DNDs in amounts sufficient for real large-scale production [2]. Naturally, this has led to sharp increase in the number of both scientific publications and proposals for use of the new material [3–5].

Like any ultradispersed substance, nanosized diamond particles are characterized by high surface activity. Reduction of surface activity and equilibration are attained via spontaneous aggregation of primary DND grains into larger clusters and their accumulation on the surface of ambient substances, i.e., products of explosive decomposition. It is also quite probable that the adsorption layer contains components of a medium which surrounds nanoparticles during their storage.

The formation of DNDs involves successive association of nanoparticles whose properties may be described in terms of the quantum mechanical theory. Primary DND crystals are valence- and coordinatively unsaturated, and their aggregation gives rise to various supramolecular complexes, mostly fractal clusters. By reaction with the environment the emerging DND clusters coordinate ambient substances, i.e., different allotropic forms of sp^2-hybridized carbon.

The procedure for the isolation of DNDs from the explosion products implies their treatment with strong oxidants, followed by washing with water. A predictable result of the action of strong oxidants on DND is the presence on their surface of functional groups having a labile proton.

The practical potential of DNDs is largely determined by their surface parameters. Intended chemical modification of DND surface could endow diamond nanoparticles with specific properties necessary for their final application.

Some practical uses require distribution of DND-modifying additives in nonpolar medium. However, their surface layer is enriched in groups having a labile hydrogen atom, so that the surface is hydrpophilic

Amount of labile proton-containing groups (mmol) per gram of DND depending on the surface preparation technique

Sample	Initial	Vacuum drying	Freeze drying
ASUD-99	2.78	0.43	2.94

Fig. 1. Sol–gel distribution of ASUD-99 detonation nanodiamonds in toluene.

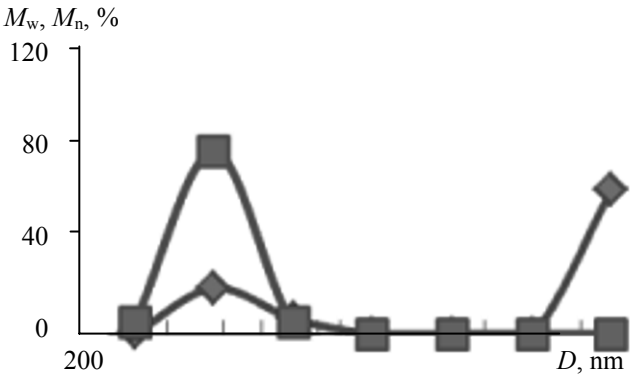

Fig. 2. Polydispersity curves of the toluene sol fraction.

[6–8]. As a result, it is impossible to obtain stable DND dispersions in hydrophobic media without surface modification. Some procedures for surface functi-onalization of DNDs to make them hydrophobic were described by us previously [9–11].

However, it should be noted that even most advanced purification procedures do not ensure complete absence of sp^2-hybridized carbon impurities. The nature of the latter is a matter of discussion. Some model concepts imply incomplete generation of the surface of DND crystals due to the nature of detonation synthesis or, by analogy with natural diamonds, the presence on the DND surface of carbon dimers (so-called Pandey chains). Apart from conditions of synthesis, the surface and hence dielectric properties of DND are determined by other factors. S. Battsanov demonstrated a sharp increase in the dielectric constant ε upon contact of DND powder with vapor of polar liquids. Therefore, preparation of DND surface remains so far an important problem. While analyzing promising lines in post-synthetic purification of DND from various impurities, we focused on a model proposed by V. Danilenko for the formation of DND particles by detonation synthesis. The model presumes that a part of DND clusters is stabilized by embedded graphite chains. In keeping with this model, complete removal of sp^2-carbon impurities from DND by surface treatment with oxidants is difficult. Furthermore, as might be expected, oxidative purification gives rise to zeolite-like monomolecular water layer which additionally stabilize DND clusters via interfacial hydrogen bonding. It should be emphasized that the sp^3/sp^2-carbon ratio (including latent carbon[1]) in DND clusters depends on the detonation and purification technologies used by particular manufacturer; naturally, this hinders their standardization from the viewpoint of application in microelectronics.

In the present work we made an attempt to purify DND from latent carbon. As subject for the study we used ASUD-99 detonation nanodiamonds manufactured at the Institute of Superhard Materials (Kiev, Ukraine). Experiments were carried out as follows. A sample of DND was kept in contact with water vapor. It was then frozen with liquid nitrogen and dried under reduced pressure. The resulting sample was divided into two parts one of which was placed in water, and the other, in toluene. The suspensions were subjected to ultrasonic treatment, and the sol and gel fractions were separated by decanting.

We anticipated that at least most part of clusters containing latent sp^2-carbon will be decomposed. In this case, the sol fraction of the aqueous suspension

[1] By latent carbon we mean carbon included in DND clusters that do not decompose under standard purification conditions.

should contain sp^3-carbon, i.e., DND, while the gel fraction should contain sp^2-carbon. By contrast, the toluene sol fraction should be enriched in sp^2-carbon, while DND should stay in the gel.

The results confirmed our expectations. The sol from the aqueous suspension had a grey color typical of pure DND suspension, while the amount of the gel fraction was insignificant. The toluene sol was dark, and most part of the sample resided in the gel fraction (Fig. 1). The weight of the decanted aqueous sol was 88.2 wt %, and it satisfactorily matched the weight of the toluene gel (86.5 wt %). Therefore, we can state with certainty that the used procedure ensures efficient isolation of latent carbon as a separate phase whose weight may be estimated at 12–14%. Taking into account that these results were likely to be obtained for the first time, it was interesting to estimate the dispersity of latent carbon particles. The data obtained by dynamic light scattering for the toluene sol are given in Fig. 2.

Analysis of these data showed that the highly dispersed component (300–1000 nm) constitutes 30 wt %. However, the size of most particles corresponded to a micrometer level. Presumably, these are stable "inverse" particles, i.e. those containing mainly amorphous carbon. Undoubtedly, it was interesting to elucidate how the DND preparation process affects the concentration of surface groups containing a labile proton. For this purpose we applied the Chugaev–Tserevitinov technique. The results are given in table.

It is seen that vacuum drying of DND (80°C) appreciably reduces the concentration of groups having a labile proton. By contrast, preliminary freezing followed by vacuum drying even leads to some increase in the amount of such groups. Presumably, vacuum drying removes only adsorbed water from the DND surface. Crystallization of the adsorbed water followed by vacuum sublimation considerably reduces the number of stabilizing interfacial hydrogen bonds with subsequent decomposition of loosest aggregates, so that hydroxy groups are removed from the bulk cluster and a new surface is formed.

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