

SURFACE STRUCTURAL GROUPS IN DETONATION DIAMOND POWDERS AND  
PROPERTIES AS DETERMINED BY FTIRDimitar Mitev<sup>1</sup>, Rayna Dimitrova<sup>2</sup>, Svetla Popova<sup>2</sup>, Stavry Stavrev<sup>1</sup><sup>1</sup>Space Research Institute - Bulgarian Academy of Sciences<sup>2</sup>Institute of Organic Chemistry - Bulgarian Academy of Sciences  
e-mail: dpmitev@yahoo.com**Keywords:** Nanodiamond, Purification, Surface peculiarities, Detonation synthesis

**Abstract.** The presented work shows the influence of several methods for final acid purification and post-purification procedures (deep freezing, microwave and furnace drying, milling) on the surface peculiarities of detonation synthesized nanodiamond. Methods of FTIR-spectroscopy and pH-measurement were applied to compare the surface functional groups.

Ultradisperse diamond powder (UDD) with nanoscale dimensions are produced by detonation of carbon-containing explosives under conditions of negative oxygen balance [1]. UDD exhibit unique properties because of their particle size, which is considerably smaller than the size of most other types of synthesized diamond, and the specific conditions of its formation. Its surface and interior structure is still a matter of debate. The information regarding the UDD microstructural properties and its component molecules is important to the overall understanding of UDD interactions and the development of novel strategies for its application. There is a variety of methods, which can be used or adapted for determining the UDD properties. These range from relatively simple and inexpensive methods to rather complicated laser light and X-ray scattering techniques. The latter provide important information but are not suitable as express methods for everyday work. Infrared spectroscopy is the study of transitions within the energy levels of a molecule, due to the absorption of infrared radiation of the electromagnetic spectrum. The frequencies at which a molecule absorbs infrared radiation are a characteristic property of its structure. In the paper, we studied UDD samples that differ by the final acidic purification, ball-milling, microwave or thermal treating.

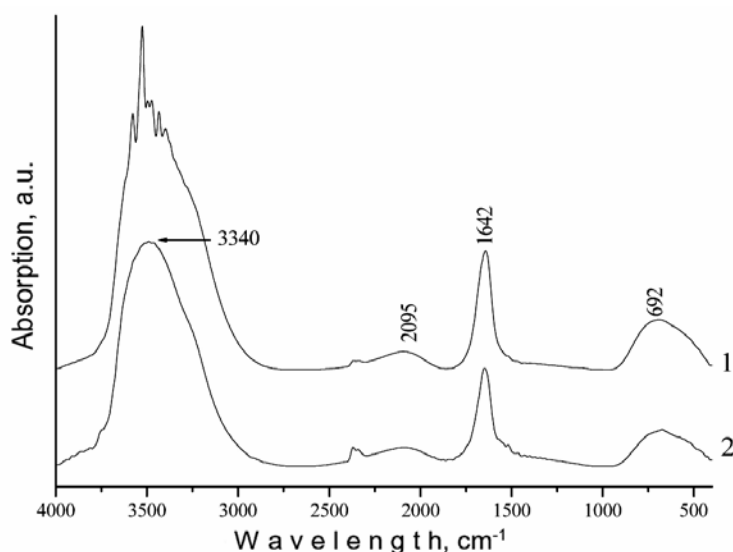


Figure 1. Nanodiamond suspensions, finally purified with HCl/HNO<sub>3</sub>  
1- not frozen, not sonified (pH 3.80)  
2- frozen, sonified (pH 3.60)

Samples structural-mechanic relationships were characterized through experiments, including N<sub>2</sub> sorption, pH measurements and FTIR spectra. Applying these simple methods, the surface chemistry of the UDD samples was shown to retain a memory of the purification conditions [2]. Generally, diamonds with more amorphous sp<sup>3</sup> bonded carbon and nitrogen-oxygen complexes on its surface are produced by the use of microwaves, HCl/HNO<sub>3</sub> acid and when TNT is the only carbon material used for detonation.

1. (Figure1): The process of the alternative three-fold freezing and sonification of the suspensions provides the necessary conditions for production of diamond powders with high quality. In the untreated suspension (line1), the diamond particle carries electric charges because of the absorption of ionization ions (strong sharp peaks in the region at 3200-3700 cm<sup>-1</sup>).

During treatment, preferential substitutions of the ions and formation of functional groups occur (line 2). The very strong absorption peak around 3440 cm<sup>-1</sup> is induced by the stretching O-H or /and N-H vibration. The absorption peak centered at 1642 cm<sup>-1</sup> is also due to the combinational action of C=O, N-H/or C-N, or C-N=O functional groups. The method of freezing/sonification shows positive influence on the nanodiamond quality, and can be recommended as additive treatment.

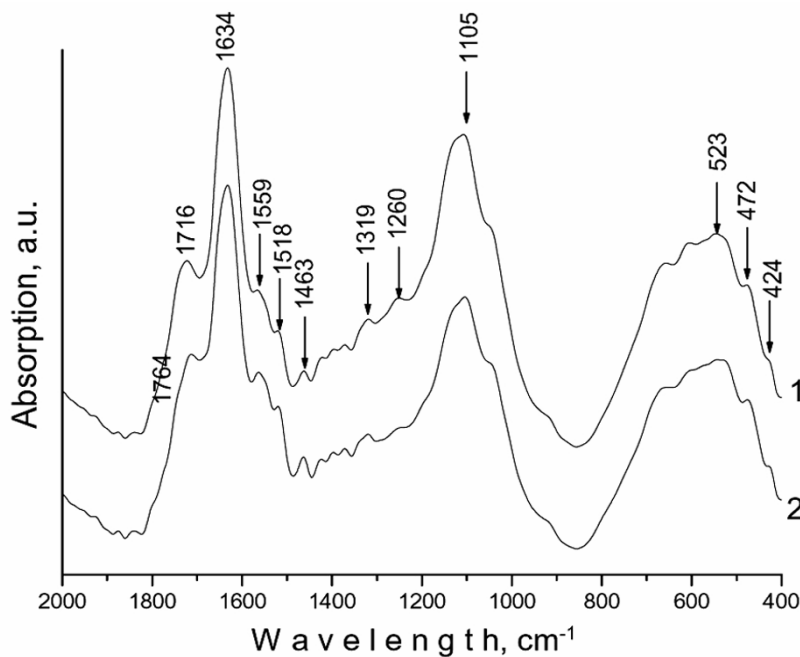


Figure 2. Nanodiamond powders (flakes)  
 1- purified finally with HCl/HNO<sub>3</sub> (pH 3.83)  
 2- purified finally with HCl (pH 4.12)

2. (Figure2): We adopted two agents for final removing of the metal impurities from the diamond particles: nitric-hydrochloric acids mixture and hydrochloric acid. The most characteristic features of the diamond particles finally purified by the different oxidizing agents are displayed in the absorbance around 1716 cm<sup>-1</sup> that is the carbonyl groups. The amount of the latter is higher for sample treated with HCl/HNO<sub>3</sub> (line 1). The absorption peak at 1764 cm<sup>-1</sup> may be connected with distinctive absorption of carbonyl for carboxyl group (line 2). So the final oxidative acid treatment is irreplaceable for removal of some metal impurities (as Cu), but changes the surface to some extent in chemical aspect.

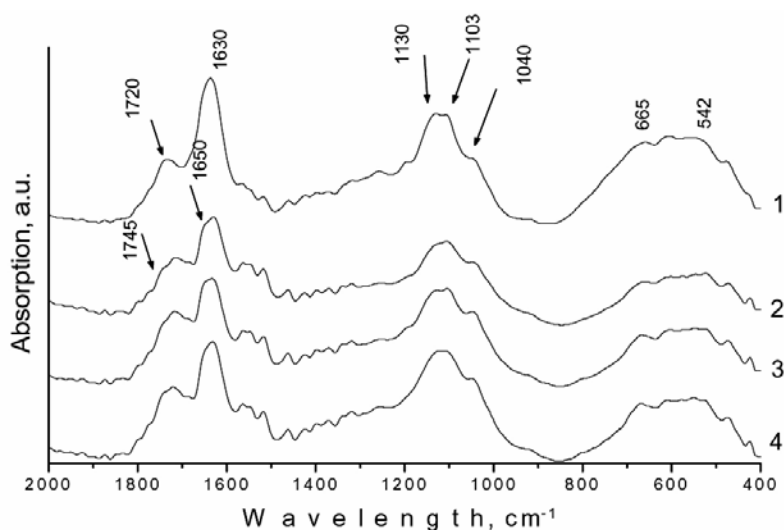


Figure 3. Nanodiamond powders, finally purified with HCl/HNO<sub>3</sub>

1- milled

2- milled, microwave heated (pH 4.09)

3- milled, furnace heated at 200 (400)<sup>o</sup>C (pH 3.80)

4- powder obtained from frozen and sonified suspension via furnace drying at 200 (400)<sup>o</sup>C (pH 4.47)

**3.** (Figure 3): - broad band at 400-700 cm<sup>-1</sup> region is correlated with the existence of N, CN, CO, CH bonds and impurities of non-carbon nature (Fe, Ni). They exist in greater extent in sample (line 1).

- the unresolved bands in the region ca 1250-1400 cm<sup>-1</sup> in the spectra of all diamond materials are due to C-C vibrations of the sp<sup>3</sup>-hybridized diamond lattice interacting with impurities or structural defects [3].

- during the microwave treatment, a diamond surface modification occur, that results in a formation of surface acidic functional groups (the peaks in the region 1400-1800 cm<sup>-1</sup> (line 2), most probably because of diamonds particle fragmentation. Based on the comparison of the intensity among the peaks can be concluded, that there are less -NH<sub>2</sub> groups and more -COOH groups on the nanodiamond surface (pH 4.09).

The diamond particles obtained from frozen and sonified suspension via furnace drying at 200 (400)<sup>o</sup>C have less surface groups. So the "diamond character" of their surface is more distinctive (pH 4.47).

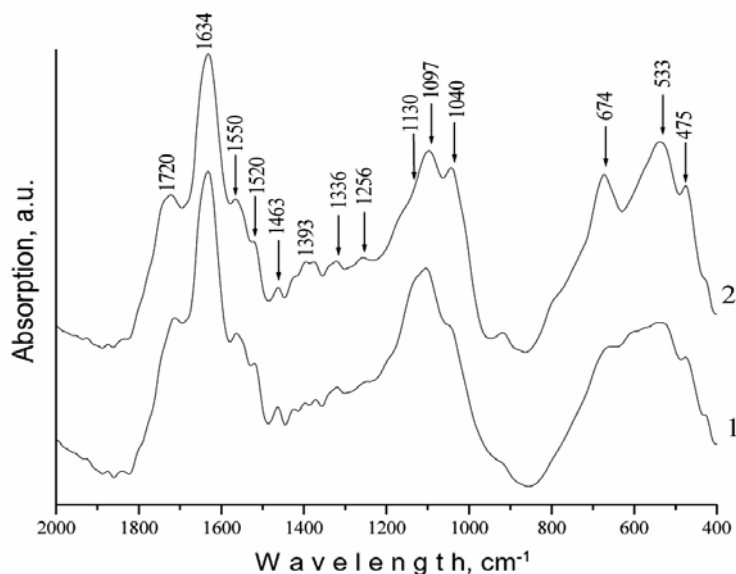


Figure 4. Nanodiamond powders (flakes), finally purified with HCl

1- obtained from TNT/RDX – same as "2" on Fig.2 (pH 4.12).

2- obtained from TNT (pH 6.20).

4. (Figure 4): As seen from the IR spectra, there is an increase in the relative content of graphitic carbon in the case of TNT-produced sample ( $400\text{-}700\text{ cm}^{-1}$  and region around  $1000\text{ cm}^{-1}$  related to C-N vibration of amines on the nanodiamond surface). The decrease of surface oxygen species and the increase of CH species imply the enhancement of the hydrophobic property of the diamond surface. Therefore, the amounts of adsorbed water are less in the sample prepared by TNT (pH 6.20).

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**References:**

1. Dolmatov V. Yu., M. V. Veretennikova, V. A. Marchukov, and V. G. Sushchev. Currently Available Methods of Industrial Nanodiamond Synthesis. *Physics of the Solid State* **46**, 4, 2004, pp.611–615
2. Mitev D., R. Dimitrova, M. Spassova, Chr. Minchev, S. Stavrev: Surface Peculiarities of Detonation Diamonds in Dependence of the Purification Methods, *Diamond and Related Materials* **16**, 2007, pp.776-780
3. Dandekar A., R. T. K. Baker, M. A. Vannice. Characterization of activated carbon, graphitized carbon fibers and synthetic diamond powder using TPD and drifts, *Carbon* **36**, 1998, pp.1821-1831