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Modification and functional properties of detonation nanodiamond

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ABSTRACT

Original termination of the detonation nanodiamond (DND) was changed by active chemical media interaction. Oxidation in boiling chloric acid, by hydrogen and chlorination by carbon tetrachloride vapor was applied. FTIR, TGA, and photoluminescence techniques revealed the DND functional termination changing. At hydrogenation treatment monofunctionally of the surface demonstrated. The totality of presented results demonstrates the possibility of substantial and controlled changes in the DND functional properties, for their subsequent use in the self-organization processes, at nanocomposites preparation and for other aims.

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KEYWORDS
Particulate nanodiamond; oxidative; chlorinating; hydrogenating treatment; monofunctionality

1. Introduction

Detonation nanodiamond (DND) is one of the most important nanomaterials. Opening of the technology and industrial production was first performed in Russia.[1,2] DND is thermodynamically metastable, and it differs from other powder materials by lack of the nanoparticle surface any other phase formations. Having crystalline diamond core, the surface of its nanoparticles presents diversity of chemical functional groups. Depending on the synthesis conditions and subsequent treatment individual DND particles comprise at their surface hydrides, ethers, carboxylase, aldehydes, lactones and other groups. Therefore, when working with DND as a ready nanomaterial there are possibility, in comparison to well-known vertical strategies in nanotechnology (bottom-up and top-down), one can follow to research and development strategy, which may be called the horizontal or "flank" strategy (Figure 1).[3,4] According to the Figure 1 only one way to manage the uncountanable number of the individual DND particles is surface functionalization for their preparation toward to a following selforganisation, in nanocomposite addition, etc. It is especially actual for the real DND powder with the size of individual crystals in the 4 to 5 nm range.

2. Experimental details

It is preferably carried out using boiling in an aggressive liquid. Supplied by SINTA Co (Minsk, Belarus) product was purified by phase non-carbon impurities and treating the precursor source – detonation soot SHA-A in 60% HNO_3 at 90 atm and 250 °C. This process allows to remove at the same time from the charge – primary synthesis product non-diamond carbon, and the majority of non-carbon impurities (Fe, Cu, Zn, etc.) with formation of soluble nitrates. Industrial similar method has been used on a laboratory scale – through a long, up to 5 hours, boiling the detonation soot in 72% $HClO_4$ at 203 °C. Thus, in the powder nearly 50% non-diamond carbon was removed and subsequent washing with distilled water followed by repeated centrifugation, allowed to reduce the content of non-carbon impurities (mainly iron) to less than 0.2 wt.%.

3. Results and discussion

Apparently, prolonged treatment effective oxidant chloric acid provides formation on the surface of the beam predominantly oxygen-containing functional groups (carboxyl, alcohol, ketone). The use of other methods – preferably by reacting at elevated temperature with gas and fluids of different composition, carried out in the apparatus described previously.[3,4] In this case, the functional properties have undergone a radical change. High-temperature gas treatment protocols were as follows:

- heating in a flow of pure hydrogen or deuterium at 850 °C, 5 hours.
- heating at 450 °C CCl_4 vapor atmosphere (4 mol. % CCl_4 in high purity Ar stream flowing over the surface of the powder at a rate of 1 cm^3/c).

Hydrophilicity of the DND samples was measured by the rate and level of weight set preheated for 20 min at 150 °C in air sample, and after placed at 25 °C in an air atmosphere

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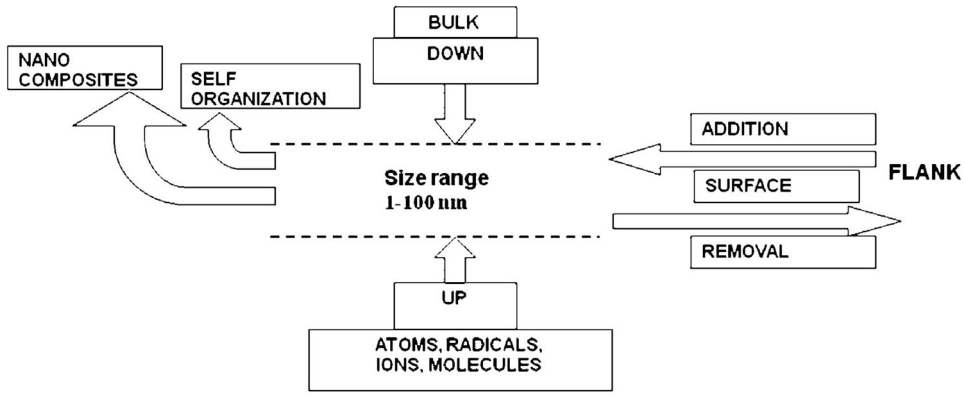

Figure 1. Vertical and horizontal strategies.

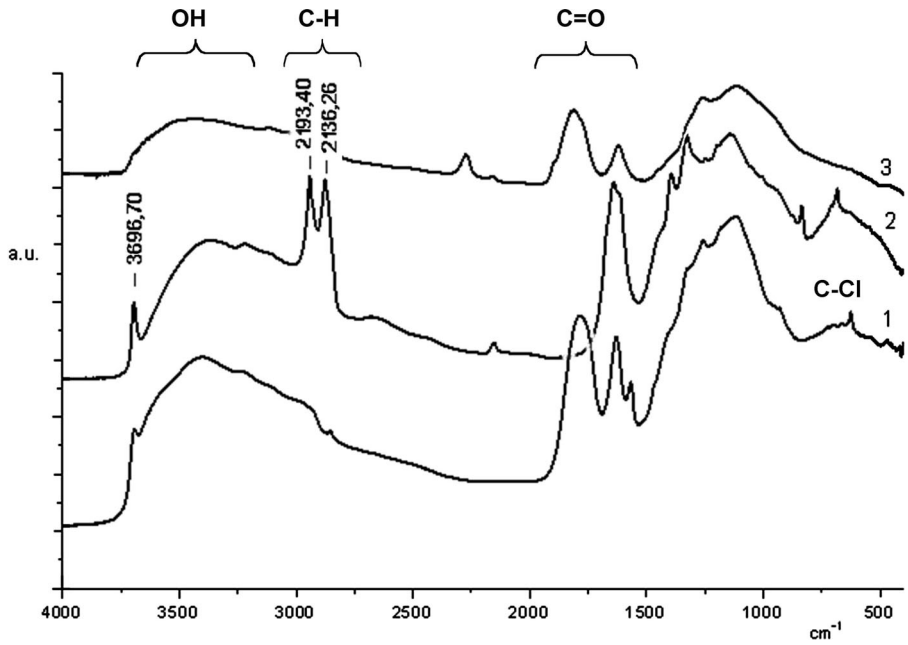

Figure 2. Hydrophility of the DND: 1 – oxidized, 2 – hydrogenated, and 3 – chlorinated.

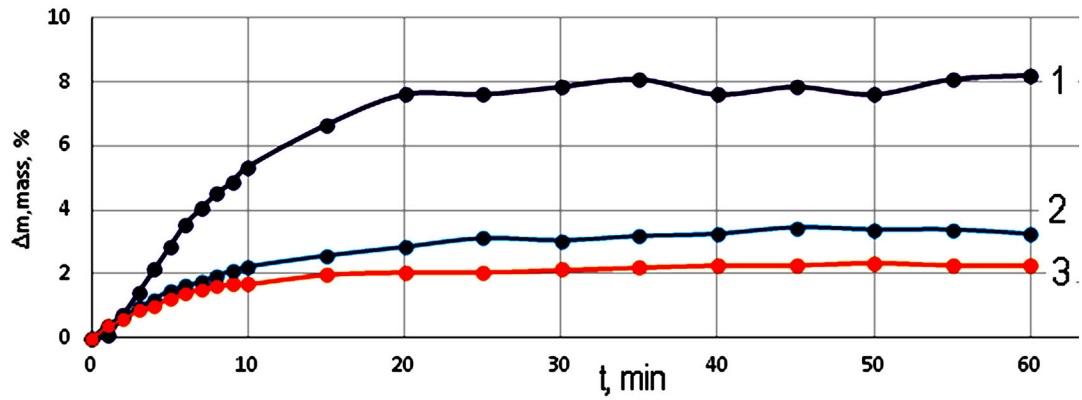

Figure 3. FTIR spectra of the DND: 3 – oxidized, 2 – hydrogenated, and 1 – chlorinated.

with a relative humidity of 60%. This level of relative humidity have negligible change with temperature, since it was created and maintained via vaporizers filled with a saturated aqueous solution of ammonium nitrate situated inside a closed volume in an analytical balance VLA-200-M. Part of the result presented in Figure 2, shows that the nature of the DND surface can change from hydrophilic to partially hydrophobic. These results were confirmed and correlated with IR spectroscopy data obtained FTIR mode (Figure 3). By reducing the content of hydroxyl groups in both the hydrogenation and, in particular at chlorination reduces the water vapor adsorption through the formation of hydrogen bonds.

Measuring the mass of samples change in the TGA heating mode at 50 °C/min in air and in high purity argon

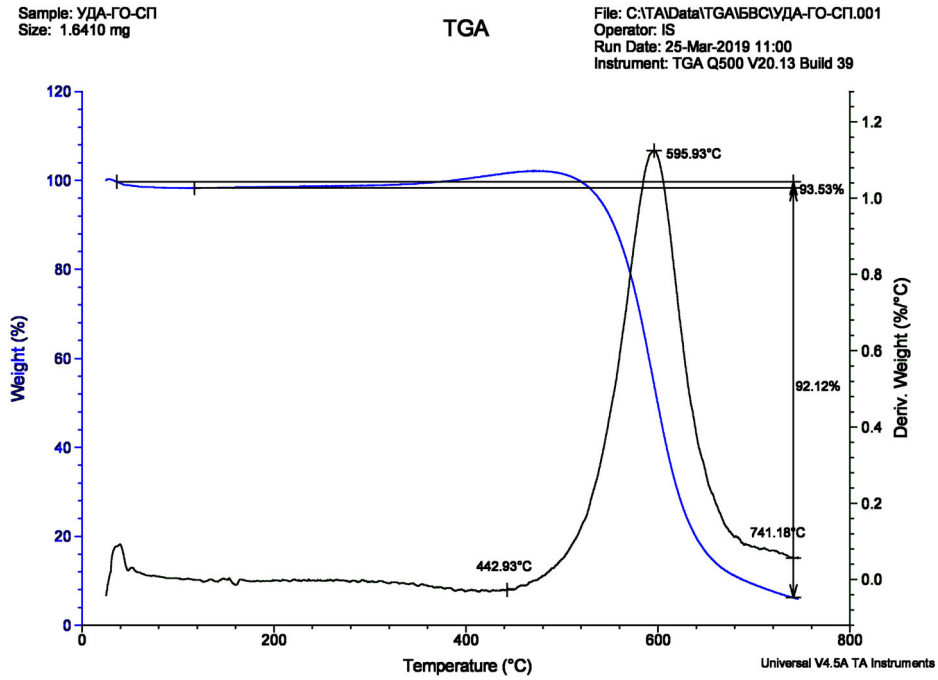

Figure 4. TGA plot of the hydrogenated DND.

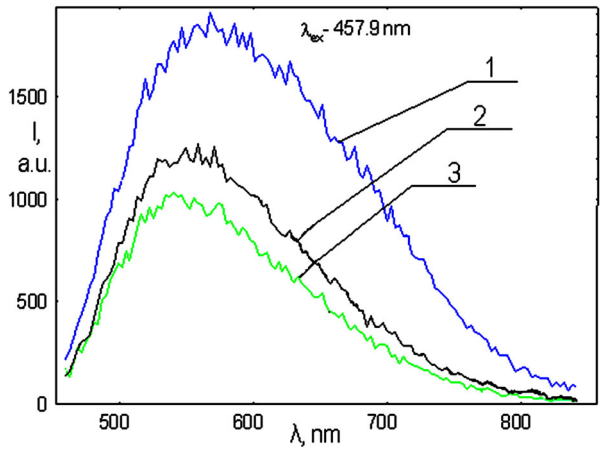

Figure 5. Photoluminescence spectra of the functionalized DND: 1 – oxidized, 2 – chlorinated, and 3 – hydrogenated.

possible to marked differences of all kinds of test samples have been established. First of all, significantly change in the beginning of temperature of oxidation. Its maximum value is hydrogenated in the sample one can see at Figure 4. Differential recording TGA curves plotted in an inert gas atmosphere shows a significant reduction in the degree of surface polyfunctionality especially for the hydrogenated DND sample (Figure 4).

Photoluminescence as a special functional DND property is currently very popular for the purposes of biology and medicine. As the least toxic of all the carbon nanomaterials DND is convenient and desirable platform for the delivery of physiologically active agents for the diagnosis and even for therapy of various diseases.

The measurement of photoluminescence was carried out on U-1000 instrument under comparable conditions (fixed excitation wavelength – 457.9 nm, the intensity of the irradiated area of the sample). The results show some variability in the maximum position in the PL intensity and the highest intensity at its hydrogenated sample DNA (Figure 5).

DND electrical properties with different surface-termination differ for difference samples drastically. Most the important is enhanced electrical conductivity of hydrogenated samples. It has semiconductor nature probably like subsurface semiconductor conductivity of CVD diamond films. It is remarkable that much more conductive detonation soot have metallic temperature dependence its electrical conductivity. Those phenomena need careful further research.

4. Conclusion

The totality of presented results demonstrates the possibility of substantial and controlled changes in the DND functional properties, for their tentative subsequent use in the self-organization processes, at nanocomposites preparation and for, other aims.

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