# NATURE OF THE SURFACE OF DETONATION NANODIAMOND AND ITS SOME FUNCTIONAL PROPERTIES

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**Abstract**

The main reason of not gained interest of researchers to the detonation-synthetized nanodiamond (DND) particles is a simplest carbon nanomaterial. The surface of its particles hasn't oxide phase and is multifunctional that allows to carry out the directed chemical modifying of its surface. Commercial DND has essential features which limit its application in nanobiotechnology. In this work, the directed chemical modifying of a surface of commercial DND produced by Sinta (Minsk, Republic of Belarus) is carried out. The DNDs with the amine-, chlorine-group, and partially graphitized surface were synthetized. Its physical and chemical properties, including ζ-potential are investigated. In wide pH-range the DNDs with oxidized surface have exhibited high sedimentation stability in aqueous solutions. For the purpose to use the chemical-modified DND in biotechnological or medical applications, the assessment of its ability to sorb viruses has been carried out. The HA titers of influenza viruses decreased in 8 till 500 times after contact with sorbents. The toxic properties of the chemical-modified DMD on cotton rats have been estimated. The Assessment of embryo toxicity, teratogenicity and mutagenicity has been carried out on Zebrafish (Danio rerio).

**Keywords:** detonation nanodiamods, sorption, influenza viruses

## 1. INTRODUCTION

The DND synthesis lasts less than 1 ms, but after removing from primary detonation soot (SHA) nondiamond and noncarbon impurities particulate nanodiamond still presents industrial semi-product and need directional “upbringing”. It does mean to use not only well-known up- and down- vertical strategies, but also horizontal or “flank” strategy in R&D (Fig. 1) [1]. The former permit to prepare intentionally nanoparticle surface for following application in course self-organization, by nanocomposite production, etc. Such kind manipulation looks not very easy due to extremely size of individual nanodimond particles (Fig. 1). But solving above mentioned and other nanotechnological issues facilitate real nature of nanoparticle surface. It ruled actually by 2D-organic chemistry and may be change by known gas and liquid phase chemical reactions.

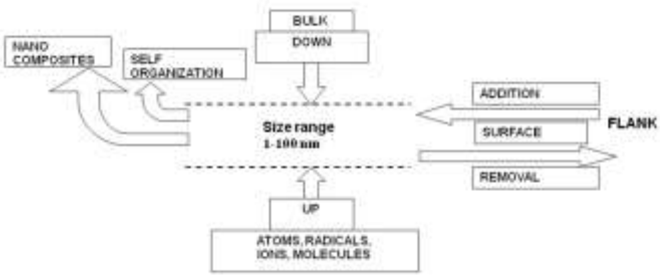


**Fig. 1.** Strategies in the Nano-Materials R&D [1].

In this work, the physical-chemical, a biological property of synthesized modified DND and its sorption ability to virus's particles has been investigated.

## 2. EXPERIMENTAL

For directed modification of surface, the soot (SHA) – initial product of detonation synthesis of DND, UDD-SP and UDD–GO-VK, produced by «Sinta» (Minsk, Belorussia), graphitized DND ($DND_{GRAP}$), chlorinated DND ($DND_{Cl}$), aminated DND ($DND_{AMIN}$) were used. The $DND_{GRAP}$ have been obtained by the heating within 1 h in the ultra-high purity argon (UHP Ar) atmosphere at 1000 °C. The $DND_{Cl}$ have been produced by the heating within 2 h of a steam-gas mixture of $CCl_4$/Ar (3 mol. % $CCl_4$) at 450°C. In order to synthesized $DND_{AMIN}$, the $DND_{Cl}$ have been heated within 1 h in the high-purity $NH_3$ atmosphere ($T$ = 1000 °C, $p$ = 1 atm).

For establishment of character of surface acidity character comparative study different carbon adsorbents, measurements of pH in water or 0.9 mol·$L^{-1}$ NaCl solution in pH – $t$ coordinates was carried out.

Colloid solutions of DND were obtained via following procedure. A 0.5 mg DND was solved in 50 ml of 0.15 mol·$L^{-1}$ NaCl solution. Then, the solution was sonicated within 20 min and centrifuged at 3000 rpm within 15 min. All solutions were prepared in distilled water, which was additionally deionized with an Arium setup (Sartorius, Germany) and had a conductivity of no higher than 0.056 μS·$cm^{-1}$.

Nanoparticle sizes and zeta potential were determined in the colloidal solution by dynamic light scattering technique (DLS). The measurements were carried out on the Delsa$^{TM}$Nano C particle analyzer (Beckman Coulter, USA) at a wavelength of 658 nm in a quartz cell at 20 °C. Previously to the measurements, suspension has been sonicated. After sonication the solution, the mean size of particles was 40 nm.

The research of sorption ability to virus's particle of DND was carried out in D.I.Ivanovsky Institute of Virology of The Ministry of Health. For this purpose, influenza viruses were incubated on chicken embryos. After incubation, viruses were concentrated with centrifugation in 0.15 mol·$L^{-1}$ NaCl solution at 26000 rpm on Beckman L5-50 centrifuge. The sorption time and temperature (4–36 °C) were various. Presence of viruses at solutions was defined in hemagglutination assay. Presence of viruses at solutions was defined in hemagglutination assay. Intensity of sorption was estimated on reducing of the hemagglutinating titre of a virus before interaction with a sorbent.

## 3. RESULTS AND DISCUSSION

### 3.1. Production and physical-chemical properties of modified DND.

Nanodimonds are unique material. Its surface may be to modify at high temperatures and in aggressive environments. Interaction of gas phase of different composition with DND has many benefits. Together with usual liquid superheated nitric acid elaboration used in commercial scale also laboratory gas phase methods for nondiamond carbon and noncarbon impurity removal was elaborated [2]. Initial DND surface is multifunctional [3, 4]. That's why in many cases is desirable to produce desirable surface termination. One of approaches is the DND elaboration in carbon tetrachloride vapor at ~450 C. The process take place in mixture of 3 mol % $CCl_4$ diluted at 1 atm pressure by Ar flow of 60 sccm. The goal of this part of research was to change hydrophilicity of the DND surface. We have measured the mass of $DND_{Cl}$ at RH = 60 %, stabilized by saturated water solution of ammonia nitrate. As demonstrate Fig. 2, there exist remarkable changes in water vapor adsorption with different chlorination degree. Maximal chlorine content grafted at DND surface was more 8 wt. %, were measured by laser flash analysis. Hydrophilicity of surface of DND is reduced with growth of containing the chlorine on surface.

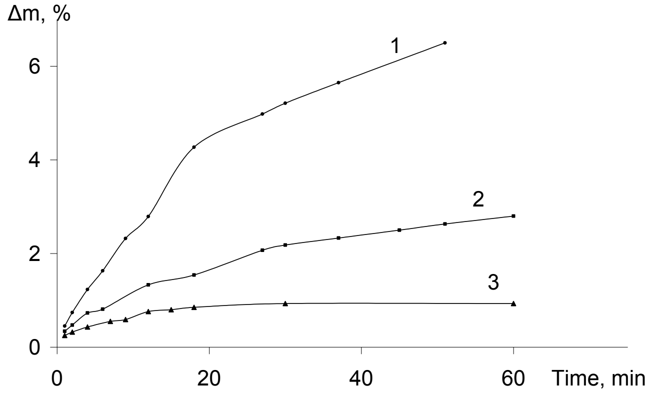


**Fig. 2.** Changes of hydrophilicity after DND have been processing by $CCl_4$ various times: 1 – UDD-SP, 2 – $DND_{Cl}$ (1 h), 3 – $DND_{Cl}$ (3 h).

For the studying surface characteristics of nanodiamonds, the dependence of zeta-potential of aqueous solutions UDD-SP («Sinta») and $DND_{Cl}$ from pH (Fig. 3) has been also studied. In both cases, a negative value of zeta-potential is observed. A decrease of pH to 3 and below, leads to its change and it strives for positive values. Such behavior may testify that a surface of DND has a negative charge. Carboxyl or lactone can give to DND a superficial charge. For $DND_{Cl}$ solution, the dependence of zeta-potential from pH has linear character in the range from 3 to 8 that can testify about higher stability of colloidal suspension (Fig. 3, curve 2). It's necessary, the range of pH is a typical for biological liquids, including for viruses solutions.

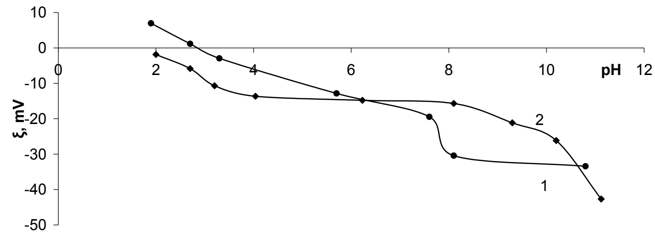


**Fig. 3.** Zeta potential-pH profile in 0.9 % NaCl solution: 1 – UDD-SP, 2 – $DND_{Cl}$ (3 h).

Adsorption of electrolytes and non-electrolytes depends on a charge of a surface of adsorbent, and the charge is in turn connected with acid-base properties of its surface. The immersion of different kind of DND into metal salts (NaCl, $CaCl_2$) solutions acidifies its surface. It implies some superficial acid group's presence. For establishment of character of surface acidity character comparative study different carbon adsorbents: charcoal, SHA, UDD-SP were studied comparatively. Figure 4 shows changes of pH in the time for various carbon materials.  It remarkable, that DND have acid surface and its p$K_1$ in the range of 1–4 situated. Satisfactory correspondence of results of definition p$K$, received by two methods (Table 1) is observed. Ionization constants (p$K_1$) acid groups in the assumption of their one-basicity at the studied types nanodiamonds lay in the range of 2 [7, 8]. Superficial groups with p$K$ = 2 can be carried to carboxyl groups, with p$K$ 5–7 can belong to a second stage of dissociation of carboxyl groups or to the lactone groups (to hydroxyacid esters).

**Table 1.** Results of calculations for p$K$.

| DND | UDD-GO-VK | $DND_{Cl}$ (UHP Ar) | $DND_{Cl}$ (Ar) | $DND_{GRAP}$ | SHA |
|---|---|---|---|---|---|
| p$K_1$ | 4.76 | 1.23 | 2.79 | 4.15 | 4.66 |

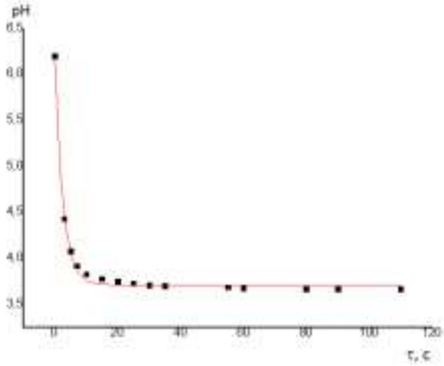


**Fig. 4.** Changes of pH in time in $DND_{Cl}$ (UHP Ar) solution.

### 3.2. Biological and sorption properties of modified DND.

Important biological property of the modified DND is an ability to sorption of biological objects, for example influenza viruses and a virus of poliomyelitis. This property defines their practical importance. Influenza viruses have an external cover which structure of surface proteins is various and depends on a species of the owner. It gives the chance, working with one virus model, to conduct researches with the viruses having differences in protein's structure. For research of interaction of DND particles with biological structures, we developed a method of an assessment of its interaction with solid sorbent. On a figure 5, the results of hemagglutination assay for influenza viruses is shown. Most intensively adsorption of viruses is observed within first 15 min of contact and didn't depend on environment temperature in the range from 4 to 36 °C. An ability of nanodiamond materials (SHA, modified DND: $DND_{Cl}$, $DND_{GRAP}$, $DND_{AMIN}$) effectively to sorb influenza viruses from water solutions, irrespective of its anti-gene properties is established. Commercial nanodiamonds (UDD-SP) produced by «Sinta» is shown low ability to sorb influenza viruses.

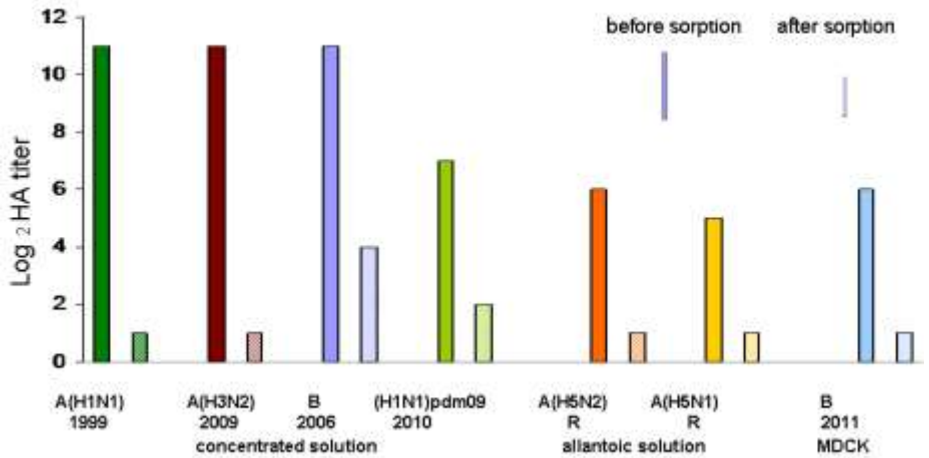


**Fig.5.** The results of hemagglutination assay for influenza viruses (Chlorinated $DND_{Cl}$).

Influence of the studied DNDs on biological objects was estimated *in vitro* and *in vivo* experiments. *In vitro* experiment was shown that cells of MDCK kept ability to a reproduction of influenza viruses A (H3N2) and B at concentration of sorbents less 0.1 $mg \cdot mL^{-1}$. After immunization of cotton rats the complexes DND-A(H3N2) in serum of blood is observed slight increase of concentration of monocytes after infusion of 2-3 mg of sorbent on a rat. Other parameters of blood remained within norm. It should be noted, that the Increase of monocytes in blood may be associated with changes of external factors of the environment, including change food, nervous stresses, etc. More details can be found in paper [9]. The assessment of embryotoxicity, teratogenicity and mutagenicity has been carried out on Zebrafish (Danio rerio).

## 4. CONCLUSIONS

It is shown that modifying of a surface of nanodiamond particles in a high aggressive gas environment leads to change of its physical and chemical properties. Thus, DNDs surface gaseous chlorination markedly more 4 times of its hydrophilicity reduced. The analysis of pH kinetic curves of different carbon materials types in water and in 1 molel sodium chloride solution permit to estimated pK of the acid centers. It is shown, that modified DND can be used such viruses sorbents.

## ACKNOWLEDGEMENTS

***The authors express appreciation to A.P.Korzhenevsky and F.N.Olesik, SINTA Co, Minsk, Belarus, for DND samples providing. This work was supported by a grant of MK-3937.2013.3; the Cooperative Agreement N 1U51│P000527-01, CDC&P, USA; RFBR 14-03-31817.***

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