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HAEMOCOMPATIBILITY OF NON-FUNCTIONALIZED AND PLASMACHEMICAL FUNCTIONALIZED DETONATION NANODIAMOND PARTICLES

HEMOZGODNOŚĆ NIEMODYFIKOWANYCH I PLAZMO-CHEMICZNIE MODYFIKOWANYCH NANOCZĄSTEK DIAMENTU DETONACYJNEGO

The purpose of this paper is to present the innovative design of microwave plasma system for modification of detonation nanodiamond particles (DNP) using a special rotating drum placed inside the reactor. Nanodiamond particles manufactured by detonation method reveal the biological activity depending on surface functionalization. Plasmachemical modification of detonation nanodiamond particles gives the possibility of controlling surface of nanodiamonds particles in biological tests. In this paper we would like to compare detonation nanodiamond (the grain sizes from 2 to 5 nm) with modified detonation nanodiamond in rotary reactor chamber, by microwave plasma activated chemical vapour deposition (MW PACVD) method in materials research (Raman and FT-IR spectroscopy) and in vitro examinations with full of human blood. The results indicate haemocompatibility of non-modified detonation nanodiamond and modified nanodiamond by MW PACVD method in rotary reactor chamber (*modified* ND-3) and the presence of haemolysis in commercial detonation nanodiamond.

Keywords: detonation nanodiamond particles, modified detonation nanodiamond, MW PACVD, haemocompatibility

Celem pracy jest przedstawienie innowacyjnego projektu systemu plazmy mikrofalowej z wykorzystaniem do modyfikacji detonacyjnych cząstek nanodiamontowych (DNP) przy użyciu specjalnego obrotowego bębna umieszczonego wewnątrz reaktora. Nanodiamontowe cząstki wytwarzane metodą detonacji wykazują aktywność biologiczną w zależności od funkcjonalizacji powierzchni. Plasmo-chemiczna modyfikacja detonacyjnych nanodiamontowych cząstek daje możliwość kontrolowania ich powierzchni w testach biologicznych. Autorzy w artykule porównali detonacyjny nanodiament (wielkość ziarna od 2 do 5 nm) ze zmodyfikowanym w obrotowej komorze reaktora, za pomocą procesu chemicznego osadzania wspomaganego plazmą mikrofalową (MW PACVD), detonacyjnym nanodiamentem. Wykorzystano badania materiałowe (Ramana i FT-IR spektroskopia) oraz badania *in vitro* na pełnej krwi ludzkiej. Badania wykazały hemozgodność niezmodyfikowanego detonacyjnego nanodiamentu i nanodiamentu zmodyfikowanego za pomocą metody MW PACVD w obrotowej komorze reaktora (zmodyfikowany ND-3) oraz obecność hemolizy w komercyjnym detonacyjnym nanodiamencie.

1. Introduction

Diamond, due to its amazing properties, is one of the most popular materials for centuries. Diamond nanoparticles find numerous applications. Currently, there is a strong interest in developing methods for nanodiamond particles modification, through which it receives the new features [1]. Diamond powders are modified by chemical , mechanical or plasma methods [2-8].

Diamond nanoparticles were produced by method described by Danilenko with modification of ampoule-free synthesis in the explosion chamber instead of ampoule synthesis. Graphite was placed directly into a cylindrical charge consisting of a TNT-hexogen mixture TG40. The charge was enveloped in a water jacket to suppress graphitization and to reduce the unloading rate of the synthesized diamond [9,10]. Shape and size of nanoparticles (2–10 nm) were inspected by high-resolution

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transmission electron microscopy. However, this images show also that nano-particles form large conglomerates [11].

Although HR TEM is able to determine the actual crystal size, such analysis is cost intensive and lacks in statistical reliability because a very limited number of particles is counted. The Raman spectrum of a perfect single – crystal diamond displays only one triply degenerated Raman line at 1332 cm^{-1} with full width at half maximum of 1,2 cm^{-1} that corresponds to the vibration of the two interpenetrating cubic lattices. The nanodiamond powders show additional peaks as a result of grain boundaries and structural defects. The intensity ratio between diamond and non-diamond phase is low in the visible range, but increases as the wavelength enters the UV range [12].

Nanodiamond particles synthesized by explosive detonation have a mean size distribution of 4-5 nm, and this detonation diamond draws considerable attention for many years. It is interesting that natural diamonds are hydrophobic, but nanodiamonds are usually hydrophilic, owing to their high surface to volume ratio and nonzero surface charge. The ND core consist of the sp^3 orbital crystal structure and the surface has the sp^2 orbital structure. Therefore, the surface contains many dangling bonds that facilitate various covalent bondings and this has drawn considerable attention for many years in gas phase. The results show that the surface-functionalized nanodiamonds are highly dispersive and stable in solution and thus, their direct use or further modifications for bioconjugation look promising [13].

Functionalization of three different types of nanodiamonds can be performed by using a cold plasma discharge generated with fluorine containing gas. Fluorination of nanodiamonds allowed previously unavailable colloidal suspension in anisole [14].

Physical and chemical properties of nanodiamonds synthesized by detonation (for example: chemically active surface area) provide a basis for predicting their possible applications in biology and medicine. Detonation nanodiamond particles can be used as an adsorptive material to fulfil practical biochemical tasks such as extraction and purification of proteins from recombinant sources (for example: *E.coli* bacterial cells) and natural object. Nanodiamonds can be used in protein chemistry as a new adsorbent for effective extraction and purification of proteins [15].

Bone marrow is the central organ which is responsible for haematopoiesis in adult people' haematopoiesis is the continuous process. The result of this process is the formation from the stem cell in bone marrow to the specialized cell presence in peripheral blood. The erythrocyte membrane is cell membrane fluidity. The molecules of water can easily go into and outside the cell. Haemolysis is the process in human body, which is connected with damage of red blood cells, that results in shortening its life time. The reasons of the first type of haemolysis are the defects in erythrocyte membrane skeleton. This type of damage of erythrocytes is the haemolysis caused by factors in the same red blood cell. These damages are connected with the inborn changes in cell membrane structure and its enzymatic system and the structure of haemoglobin. The second type of this pathological process is the haemolysis caused by factors besides erythrocyte membrane [16,17].

The presence of these factors in human organism is the symptom of many diseases. There are: antibodies, bacteria, physics and toxic factors [18].

All biological membranes contain lipids as major constituents. The four major classes of membrane forming lipids: glycerophospholipids, sphingolipids, glycosphingolipidsand glycoglycerolipids. The membranes of living cells are remarkable bits of molecular architecture, with many and varied functions. To say that a membrane is essentially a phospholipid bilayer is a gross oversimplification. Much of our current understanding concerning biological membrane is based upon the fluid mosaic model proposed by S.J. Singer and G.L. Nicholson in 1972. The fluid, asymmetric lipid bilayer carries inside a host of protein.

The results of heamocompatibility research of human blood plasma with detonation nanodiamond particles show the high biological bioactivity in contact with human erythrocyte through the inhibition of oxidative stress in and the absence of haemolysis [4]. The erythrocytes were prepared for the measurement of activity of superoxide dismutase (SOD). The results of this research can provide valuable information that may be used in the application of medical implants coated with a layer of diamond. The presence of diamond nanoparticles in the living body of a patient does not pose a threat carbon is biocompatible with living organism, and at the same time, one should be aware of diamond nanoparticles bioactivity in contact with biological material. The results of this research indicate a protective antioxidant action of diamond nanoparticles by increasing the activity of superoxide dismutase in erythrocytes (SOD) sweeping free radicals and inhibiting oxidative stress of cells, described an anti-inflammatory agent. Diamond nanopowder, produced by detonation method, changes the oxidation-reduction potential of erythrocyte membrane cell and it acts as an immunosuppressant on innate immune cells [19].

Nanocrystalline Diamond Particles, made by detonation method was used for modification of ND surface. Nanodiamond particles manufactured by detonation method reveal the biological activity depending on surface functionalization. Plasmo-chemical modificatiom in MW/PACVD rotary chamber of detonation nanodiamond particles gives the possibility of controlling surface of nanodiamonds particles in biological tests [20]. Functionalization of nanodiamonds can be performed by using a cold plasma discharge generated with fluorine containing gas. Fluorination of nanodiamonds allowed previously unavailable colloidal suspension in anisole [21]. Chemical modification of diamond nanopowder of detonative type was done using Fenton's reaction, which is carried out by placing hydroxyl groups – OH into the diamond nanopowders [22,23]. Surface functionalization of nanodiamond particles is highly dispersive stable in solution modified in oxidizing procedure and generate carboxylated nanodiamond compounds (ND – COOH) [24]. Unique properties of carbon atoms sp^3 in diamond caused the possibility of modification of nanodiamond surface. Chemically-modified nanodiamond particles are served as an HPLC [25].

The last application is the surface modification of detonation nanodiamond particles to enhance the diamond nucleation for the growth of nanocrystalline diamond films which could be used in photovoltaic application. The results of FT-IR spectroscopy demonstrated that plasma treated diamond nanoparticles possessed polar surface functional groups and attained high dispersion in methanol indeed open up a prospect of nanocrystalline diamond films in solar cell application [26].

The study of adsorption of human blood plasma on various sized carboxylated detonation nanodiamonds using UV/visible spectroscopy and Fourier transform infrared spectroscopy (FT-IR). tHe influence of carboxylated detonation nanodiamonds on the blood coagulation has been estimated using Activated Partial Thromboplastin Time (APTT) test. The APTT test results indicate that 5 and 100 nm carboxylated detonation nanodiamonds with various concentration (10-500 μg/ml) do not show delay in when coagulation was initiated through the intrinsic pathway [27].

Modification of implants on the external surface for improving haemocompatibility are based on surface –blood cell interaction between carbon, titanium and biopolymer and mouse fibroblast, platelets and HUVEC (Human Umbilical Vein Endothelial Cells). Materials were elaborated by using plasma as pre-treatment in vaccum by coating. TiN (titanium nitride), surface coating reveal high compatibility with mouse fibroblast. In fluorescent microscopy were detected the live cells. In reactions with platelets good haemocompatibility show TiN (titanium nitride), Ti (C,N) – titanium carbonitride and Si-DLC (silicone doped diamond like carbon). There were not observed aggregates on surfaces of these biomaterials. The HUVEC were deposited onto TiN (C,N) and Si-DLC. The results indicate the good cell biocompatibility of modified biomaterials TiN (C,N) and Si-DLC (survival/growth results) in compare with TiN which biomaterial reveal the absence of cell growth and survival on the surface [28].

In this study control of nanoparticles release from films were demonstrated by cytotoxic effect of silicone carbide (SiC) nanoparticles introduced by the plasma activated chemical vapour deposition (PACVD) method into poly-L-lysine/hyaluronic acid (PLL/HA) or poly-L-lysine/alginate acid (PLL/ALG) films could be controlled by chemical cross-linking of the polyelectrolyte film. The results indicate the low cytotoxic effect on cellular (mouse fibroblast L929,ATCC) viability of the silicon carbide cubic nanoparticles formed by PACVD method [29].

The chemical composition influences on the properties of the surface, particulary the surface energy, which makes the important contribution in cell-materials interactions. The silicon doped diamond –like carbon examined in haemocompatibility test based on platelet function and the scrining of primary haemostasis abnormalities reveal good haemocompatibility of this biomaterial. The next results indicate the influence of surface modification in the form of linear channels on cell behaviour. Reduced growth of smooth muscle cells was seen in the heat affected zone , but intercellular connections were formed through this zone. Final surface modification by porous coating deposition and cell –material interaction analysis show the modified surface covered by endothelial layer which is responsible for the inhibition of coagulation process. This result is very promising to obtain the biomaterial anti-coagulant and ani-thrombogenic surface [30].

The inner surfaces of polymer (silicon carbide, silicon oxide and silicon nitride) tube were covered with anti-thrombogenic coatings. The interaction s of materials with the blood and the activation of blood clotting cascade both depend on the following elements: the surface morphology, platelets and coagulation protein. After the haemocompatibility test, the surfaces of biomaterials inhibit the blood-clothing cascade and decrease the number of platelets and leukocytes [31].

Deposited Cr/CrN and TiN/CrN coatings comprised equiaxual crystallites in the range of 1 to 10 nm in the part contacting with the substrate. The buffer layer was deposited under the increasing the kinetic energy conditions by the gas flow change. It concerns the structure modification from amorphous to crystallized. Biocompatibility was regarded in aspect of biophysics and cell kinetic adhesion description. There were found differences of the shear stress values and the percentage of the detached cells between the titanium substrate surface abd the surface of the coating [32].

TiN coatings were chosen as a blood contacting material. Thin coatings of TiN can be deposited by a number of physical and chemical vapour deposition methods including evaporation, ion plating and sputtering. These materials could potentially be applicable for devices to be used within the heart chamber itself: polyurethane (PU) covered with haemocompatible titanium nitride (TiN) and pure titanium with TiN coating. Te results indicate that the pulsed laser deposition can be used to produce TiN coatings at room temperature, making it possible to fabricate fine grained and uniform layers , suitable for use in internal heart devices [33].

2. Materials and methods

The nanodiamond powders were produced by detonation methods described by Danilenko [9,10]. For investigation were selected nanopowders directly synthesized by Danilenko (ND-0) and two obtained from Adamas Company (ND-1 and ND-2) – specification of commercial nanodiamond powders is showed in Table 1. Nanodiamond powders ND-2 were plasmochemically modified in MW PACVD chamber – schematically shown in the Fig. 1. In order to modify nanodiamond from all sides, 5 g nanopowder was placed in rotary drum. Before plasmochemical modification, after pumping, the powder was annealed at 200°C for about 3 days. The conditions of MW PACVD process are presented in Table 2 – the powder after modification was described as ND-3.

TABLE 1

Technical specifications of commercial nanodiamond particles obtained from Adamas Company (ND-1 and ND-2)

Parameter	
Structure	**Cubic diamond**
Average particle size	4.0 nm
Agglomerate size in aqueous solutions	200 nm
The density of the powder	0.3-0.7 g/cm^3
SSA (specific surface area)	300-400 m^2/g
Colour	grey
Cleanliness	> 98%

TABLE 2

Parameters of MW PACVD process the modification of detonation nanodiamond powder (ND-3 powder obtained after modification)

Parameter	
Pressure	1.0 Torr (133.32 Pa)
Temperature	460°C
MW power	900 W
Process time	60 min
Atmosphere	mixture of nitrogen (78%) and oxygen (21%)
Speed of rotary drum	60 rev/min

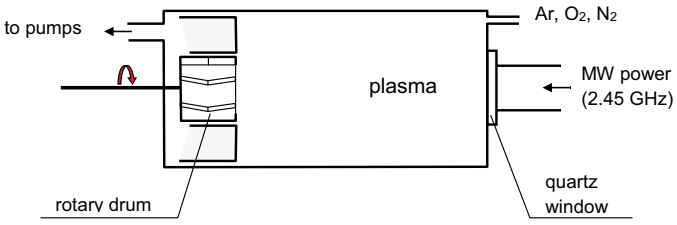

Fig. 1. Schema of MW PACVD chamber with rotary drum to modification of nanopowders

The nanodiamond powders were investigated using the Renishaw inVia Raman Microscope equipped with 532 nm laser arranged in a backscattering geometry. The power of the laser was 1.5 mW. The investigated wavenumber ranged from 900 cm^{-1} to 2100 cm^{-1}. All measurements were carried out at room temperature and in air atmosphere. Chemical and physical structures of materials were also investigated by Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) using the Thermo Scientific Nicolet iS50 FT-IR spectroscope. DRIFT spectra were collected in the range of 400-4000 cm^{-1}.

The biological tests were performed on all selected detonation nanodiamonds (clear and after modification). At beginning, powder was incubated by 4 hours in 37°C. Next 1miligram of nanodiamond powder was dissolved in 1 milliliter deionized water. The suspensions of nanodiamonds were added to samples of full human blood collected on citrate in amounts: 20 ul to 500 ul full human blood. Attempt to reference: full human blood without nanodiamonds. Histological preparations were prepared of living drop of blood and have been observed after 10 minutes in optical microscope OLYMPUS CX31 (400 times of magnification).

Blood came from volunteers from Regional Blood Center and Transfusion in Gdańsk.

3. Results and discussion

3.1. Materials results

All powders (manufactured and after modification process) were exanimate by Raman spectrometer. Collected spectra, in Fig. 2, indicated lack of difference in analyzed powder. In all spectra is observed Raman line at around 1323 cm^{-1} typical for nanodiamond particles coated by graphite phase, on which existence indicated broad G peak as well as D peak. The G peak at around 1580-1600 cm^{-1} has been assigned to the scattering by sp^2 bonded carbon associated with graphite. The D peak at around 1350 cm^{-1} is associated with the disorder due to the formation of sp^3 bonded between graphite adjacent planes [34,35].

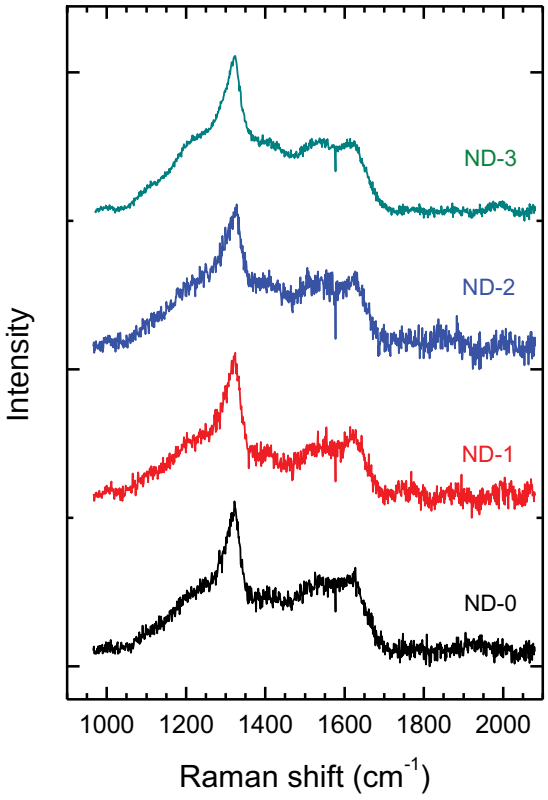

Fig. 2. The comparison of spectrum for all examined detonation nanodiamond particles in Raman spectroscopy (ND-0 “Danilenko”, ND-1 “Gdansk”, ND-2 “Koszalin”, modified ND-3 “Koszalin”)

In spectra we can also identify the peaks near 1150 cm^{-1} and near 1450 cm^{-1}. Ferrari and Robertson argue that these peaks should not be assigned to nanocrystalline diamond or other sp^3 – bonded phases. They think that these peaks are assigned to transpolyacetylene segments at grain boundaries and surface, so sp^2 configurations [36].

Fig. 3 shows the Fourier transform infrared (FTIR) spectra of all examined nanodiamond particles. As it can be seen in these figure, the all investigated nanodiamond spectra look almost the same with one small difference. In the spectra after nanoparticles manufactured by Danilenko (ND-0) appear two small peaks that are not observable in the other (from Adamas Company before and after plasmo-chemical modification). Namely, we can observe the peak at 1561 cm^{-1} and 2090 cm^{-1}, which can be attributed respectively to bonds of nitrogen with oxygen and carbon atoms.

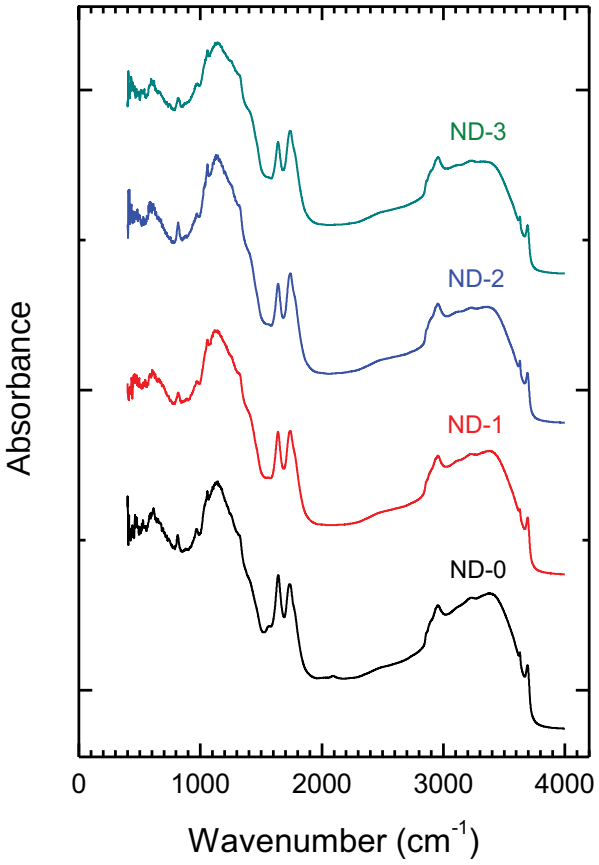

Fig. 3. The comparison of FT-IR spectrum between all examined detonation nanodiamond particles for pure nanopowders (ND-0 "Danilenko", ND-1 "Gdansk", ND-2 "Koszalin", modified ND-3 "Koszalin")

Generally, in all FTIR spectra (Fig. 3) we can observe bands at ~ 3420 cm^{-1}, 1740 cm^{-1}, 1630 cm^{-1} and ~1140 cm^{-1}. The two bands at ~ 3420 cm^{-1} and 1630 cm^{-1} corresponded to stretching mode (ν_{OH}) and bending mode (δ_{OH}) of hydroxyl groups from absorbed water [40]. The band at 1740 cm^{-1} is attributed to C = O stretching mode ($\nu_{C=O}$) and at ~1140 cm^{-1} to C-O stretching mode (ν_{C-O}) of carbonyls or carboxyl groups on the nanodaiamond surface. The presence of peak from hydroxyl groups gives the possibility to functionalization of nanodiamond particles surface by chemical and biological modifications [3, 37-39].

3.2. Biological results

Figures 4-9 show the results of biological tests with full human blood without nanodiamond particles as a control (Fig. 4) and in presence of nanodiamond particles (Fig. 5-9). Fig. 4 shows the normal human red blood cells (erythrocytes) without any damages.

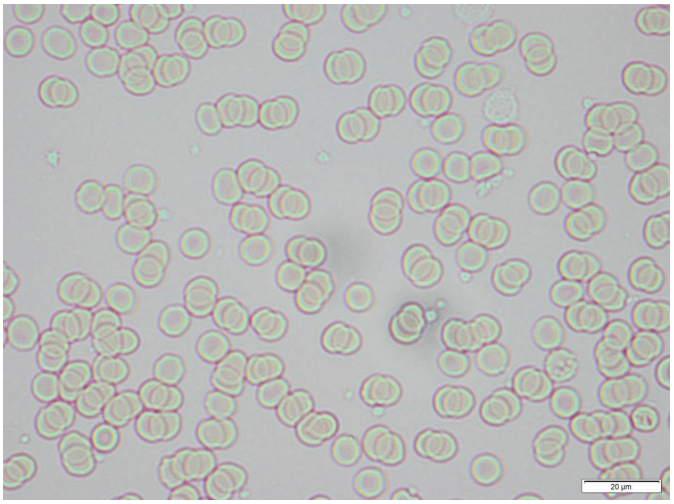

Fig. 4. The normal erythrocyte without detonation nanodiamonds particles after 10 minutes. Optical microscope OLYMPUS CX31

Fig. 5 shows the rouleaux of erythrocytes in contact with ND-0 nanodiamond particles. This is probably depending on the presence of nanodiamond particles as the biomaterial and has caused the change in shape of human red blood cells but the physiological function of these is preserved. Fig. 6 shows the agglutination of human red blood cells in contact with ND-1 nanodiamond particles. This process is connected with the reaction on the presence of nanodiamond particles agglomerates (clusters). This process can be presented in normal erythrocytes. Fig. 9 shows the haemolysis of human red blood cells in contact with

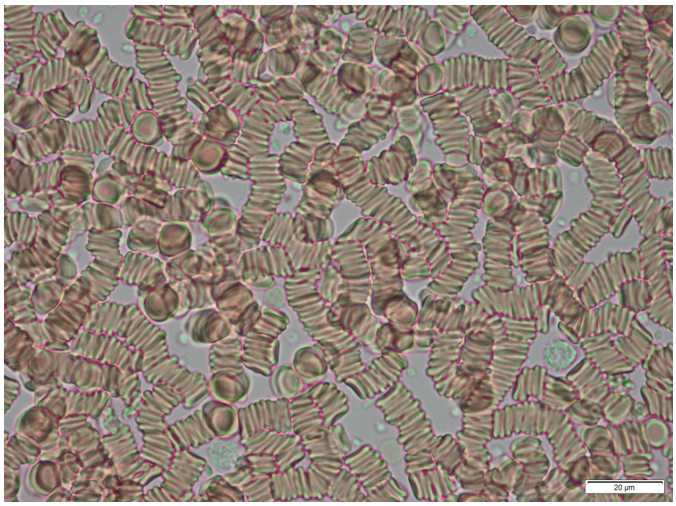

Fig. 5. Rouleaux of erythrocytes in contact with ND-0 nanodiamond particles after 10 minutes. Optical microscope OLYMPUS CX31

the presence of ND-1 nanodiamond particles. We have observed the spherical shape of erythrocytes (spherocytes) responsible for pathological image and function of blood.

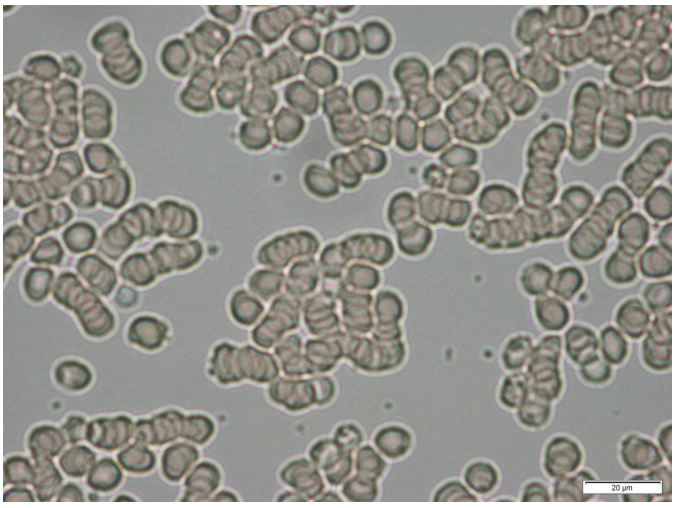

Fig. 6. Agglutination of red blood cells in contact with ND-1 nanodiamond particles after 10 minutes. Optical microscope OLYMPUS CX31

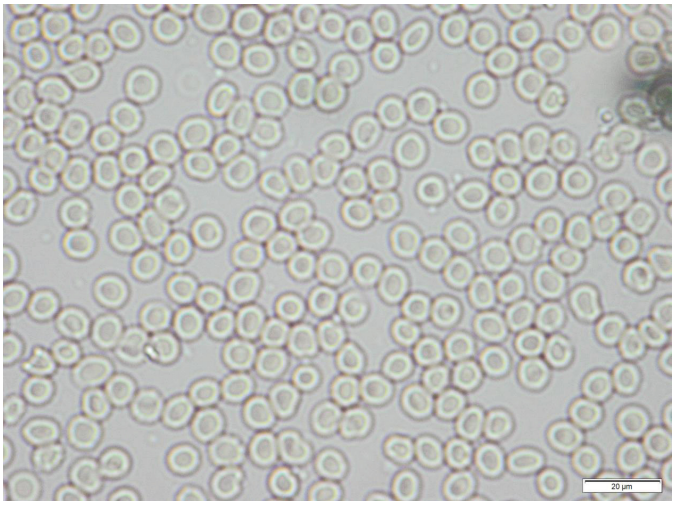

Fig. 7. The haemolysis of red blood cells (the presence of spherocytes) in contact with the presence of ND-1 nanodiamond particles after 10 minutes. Optical microscope OLYMPUS CX31

Fig. 8 shows the normal human red blood cells and the shadows of erythrocytes and the presence of schistocytes in contact with ND-2 nanodiamond particles. This blood picture corresponds to physiology of blood function. Fig. 9 shows the normal erythrocytes in contact with *modified* ND-3 nanodiamond particles.

4. Conclusions

ND modification technology MW CVD method using a rotary generator chamber may be significantly better compared to the commonly used methods of using the static reactors. This method will make it possible to carry out the modification process

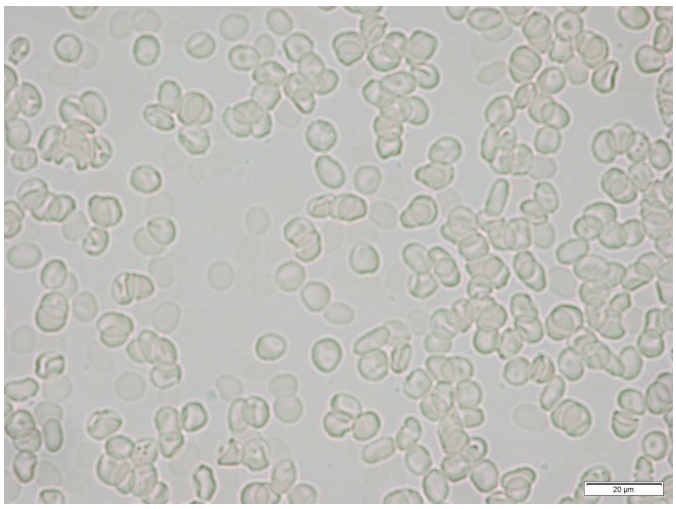

Fig. 8. The normal human red blood cells and the shadows of erythrocytes and the presence of schistocytes in contact with ND-2 nanodiamond particles after 10 minutes. Optical microscope OLYMPUS CX31

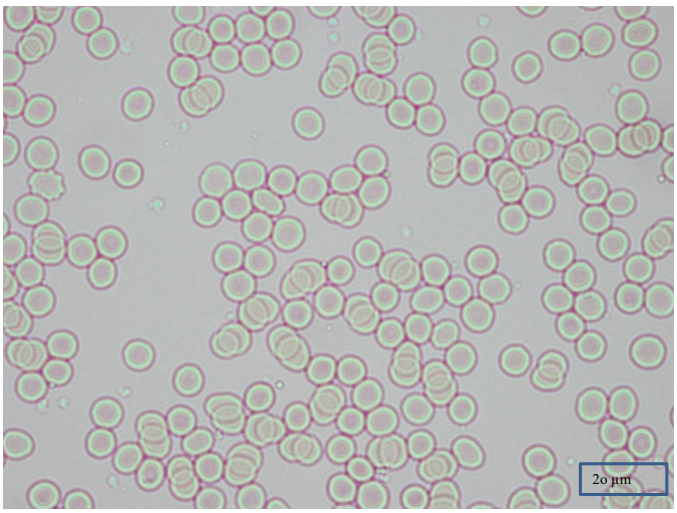

Fig. 9. The normal erythrocyte in contact with modified ND-3 nanodiamond particles after 10 minutes. Optical microscope OLYMPUS CX31

in a continuous and cyclic way (through multiple rotation of the reactor chamber), to the extent not achievable by classical methods. This will reduce costs at the same time, increase productivity and enable controlling the degree of modification of the ND.

We successfully managed to carry out the project – from concept, through preliminary design to the implementation of the microwave modification system, ND. Objectives of the project have been completed, and to the surprise of sceptics, managed to generate stable microwave plasma. Implementation of rotation within the vacuum chamber caused a lot of problems, but in the end, thanks to an innovative solution, worked. Currently awaiting the results of the first modification of the ND.

The Raman spectroscopy and FT-IR spectroscopy provided that we have used the nanodiamond particles with the presence of sp^3 and sp^2 phases. These combinations of bonds are biocompatible with human environment in vitro study.

The biological results proved the haemocompatibility of non-modified detonation nanodiamond (ND-0 from V.V. Danilenko, ND-2 from Adamas Company) and modified nanodiamond by MW PACVD method in rotary reactor chamber (*modified* ND-3) and the presence of haemolysis in commercial detonation nanodiamond (ND-1 from Adamas Company). These results are very promising for plasma-chemical modification of nanodiamond particles in biological studies.

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