Report on the execution of program 04-5-1131 -2017/2021 "Radiation Physics, Radiochemistry, and Nanotechnology Investigations Using Beams of Accelerated Heavy Ions" and proposal for the prolongation for the period of years 2022-2023

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In accordance with the Thematic Plan for JINR and the seven-year plan of development of JINR for 2017-2023, the activities under program 04-05-1131-2017/2021 were focused on the following key areas:

(1) Studies of the effects caused by heavy ions in matter, aimed at the testing the radiation resistance of materials under the influence of multiply charged ions; development of nanotechnology applications of accelerated ion beams; controlled modification of materials and the synthesis of nano-objects with unique properties for new applications.

(2) Further studies of potentialities of the ion track technique as the method to create nano- and nanoporous materials, including membranes for different separation processes; investigation of properties of symmetric and asymmetric electrically charged track-etched nanochannels; development of functional composite track membranes.

(3) Work related to life sciences: the use of track-etched membranes for analytical purposes; the use of nuclear physics methods for the environmental monitoring.

(4) Modernization of the FLNR accelerator complex and construction of new accelerators for practical applications.

In particular, the following work was carried out and the following results were obtained:

Structural response of radiation-resistant dielectric crystals (MgO, Al_2O_3, $Y_3Al_5O_{12}$) to swift heavy ion irradiation was studied using molecular dynamics (MD) and high resolution transmission electron microscopy. Comprehensive MD simulations demonstrated that despite similar ion energy losses and the initial excitation kinetics of the electronic systems and lattices, significant differences occur among final structures of ion tracks in these materials, supported by experiments. The simulations enabled us to identify recrystallization as the dominant mechanism governing formation of detected tracks in these oxides. The effects of the viscosity in molten state, lattice structure and difference in the kinetics of metallic and oxygen sublattices at the crystallization surface on damage recovery in ion tracks were analyzed [1,2].

Combination of low energy He ion implantation and swift heavy ion irradiation has been used to study helium porosity in EP450 oxide dispersion strengthened steel containing crystalline or fully amorphous Y-Ti-O nanoparticles. It was found that helium bubbles formed during post-irradiation annealing have better adhesion to amorphized precipitates compared to crystalline ones. However, this does not affect the overall porosity of the alloy which is defined by helium bubbles formed on structural defects inside the ferrite grain body and on grain boundaries [3].

The effect of swift heavy ion irradiation on the structure and properties of graphene oxide (GO) films was studied over a broad range of ion energies and fluencies. Fabrication of conductive nanosized reduced graphene oxide spots, accompanied by the formation of sp-hybridized carbon chains was demonstrated [4]. It was found that high energy heavy ion impact results in formation of graphene quantum dots (QDs) in a nonconducting matrix of graphene oxide and fluorinated graphene. Both the number density and the diameter of QDs can be tailored by a suitable choice of irradiation parameters (ion type, fluence, and energy) [5]. At the present time 2D-materials exhibiting unique properties are attracting enormous interest. They are likewise very promising for membrane applications, and therefore it is an objective of this project to explore the possibility of forming nanoporous structures in graphene and graphene oxide. A series of experiments were performed to study defect formation in these materials. Changes in electronic properties and Raman spectra have been observed and interpreted. The ultimate goal of the research is to obtain an answer to the question of the possibility of production of membranes for desalination and separation of molecules, exhibiting unprecedented performance [6]. It is planned to continue this activity in the period 2022-2023.

The study of asymmetric "track" nanopores was continued with a view to a better understanding of the behavior of fluids and solutions in nanovolumes. It was found – for the first time – that both symmetric and asymmetric track-etched nanopores with radii of 5-20 nm demonstrate well-pronounced osmotic effects in electrolyte solutions [7, 8]. These effects play an important role in the process of asymmetric etching of single tracks to be employed as nanopore sensors and can be used to control the pore geometry, which, in turn, determines the selective and diodelike properties of the asymmetric nanopores.

An example of a promising functional material on the basis of track membranes (TM) is a porous substrate for sensors working on the principle of giant combinational scattering (SERS, «surface-enhanced Raman scattering»). The combination of the membrane action with the SERS sensor function, achieves a several orders of magnitude increase in the sensor sensitivity via the concentration of the desired analyte sample by recycling through the membrane. The composite functional material that consists of a microporous substrate with a SERS-active layer of silver nanoparticles was developed and studied. Detailed data on the chemical composition and structural and morphological properties of the dispersion of silver nanoparticles have been obtained. Necessary conditions for the modification of track membranes with an intermediate layer of polyethyleneimine (PEI), which ensures effective adsorption of silver nanoparticles (AgNPs) on the TM surface, have been revealed. It was found that a TM-PEI-AgNPs composite exhibits the SERS effect with an enhancement factor of up to 10^7 for the test compound 4-aminothiophenol [9].

The technology has been developed for the surface modification of polyethylene terephthalate track microfiltration (pore size of 0.3 μm) membranes with thin (20-80 nm) films of titanium (Ti) and titanium dioxide (TiO_2) using. Ti was deposited on the roll-to-roll scale in an argon atmosphere using the magnetron sputtering method, and the TiO_2 thin films were deposited in the reactive sputtering mode in the presence of oxygen over a Ti-coated membrane substrate [10]. The structure and morphology of the obtained composite TMs were analyzed using AFM, SEM, TEM, EDS, and XPS methods. The water and gas flow rates for the composite TMs were also examined. The study showed that roll-to-roll magnetron sputtering is a viable approach to the large-scale fabrication of this new type of hybrid ceramic-polymer membranes. With these membranes inside, pilot modules for tangential microfiltration have proven themselves in the production of immunoglobulin and an influenza tetravalent vaccine.

A procedure for the production of chitosan and polyethylene oxide nanofibers by electrospinning followed by covalent bonding on Ti-coated TMs was developed [11] Biocompatibility studies of the obtained composite materials (plane membrane + layer of nanofibers) showed their applicability in regenerative medicine. Another promising TM-based composite was obtained by the electron beam deposition of superhydrophobic coatings on the track-etched membrane surface [12]. Both ultrahigh weight polyethylene and Teflon polymers were employed to create this kind of water-repellent membranes. Their structure and composition as well as the wetting properties were examined in detail aiming at exploring the applicability of these membranes to real separation processes such as membrane distillation.

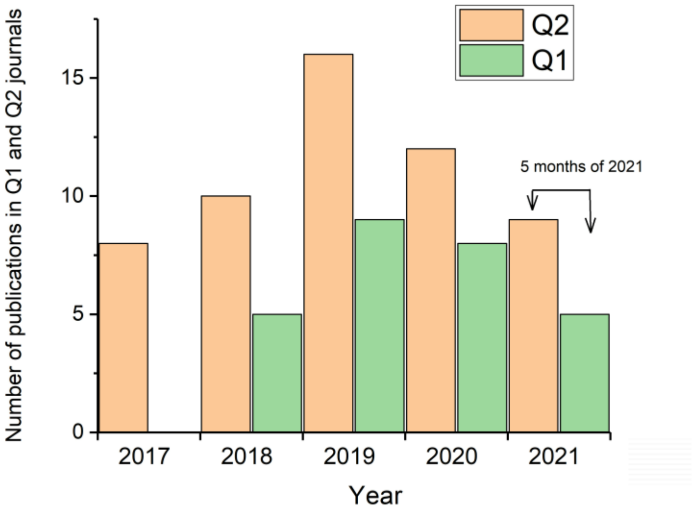
Recently it was discovered that a combination of a long exposure to ultraviolet (UV) radiation and the extraction of radiolysis and photolysis products from tracks makes it possible to create ion-selective membranes from polyethylene terephthalate (PET) films irradiated with heavy ions [13]. These membranes exhibit high selectivity for singly charged cations and high transport characteristics in the electrodialysis mode. This finding paved the way to the creation of track membranes of fundamentally different kind. In contrast to traditional microfiltration and ultrafiltration TMs, this kind of membranes is characterized by an effective pore size on the order of 1 nm and can be employed for ion separation. In order to understand the structure and the functioning of these ion-selective TMs, the process of photolysis of ion-irradiated PET and the process of nanopore formation during the liquid extraction at different temperatures and different pH were studied [14]. It was found that there are several critical parameters determining the transformation of a monolithic polymer matrix into a highly anisotropic ion-conductive structure.

In the field of radioanalytical studies, the methods of X-ray fluorescence, gamma-activation, neutron activation, gamma- and alpha-spectrometry were applied to versatile tasks, e.g. to determine the elemental composition of both the environmental samples and the artificially synthesized nanostructured materials, to support experiments on the synthesis of new transfermium nuclei [15], to study photonuclear reactions [16], and others. Further work will include the development of nondestructive methods for the examination of cyclotron targets and tests of promising target materials for thermal and radiation stability in harsh environment of nuclear physics experiments at FLNR.

Further progress of applied research requires new approaches to the strategy of development of accelerator instrumentation. *For technical, organizational and economic reasons, an optimal solution will be the creation of a new dedicated accelerator but not the exploitation of separate channels on the DC280, U400 and U400M accelerators*. The new accelerator, the DC140 cyclotron, will be significantly more powerful than IC100 (which is under operation at present) and will provide beam parameters necessary for radiation materials science, production of track membranes, testing of microelectronics, and other potential applications. The concept of this dedicated accelerator was developed in the past three years [17]. The plan for the next two years implies the creation of three specialized beam lines at the DC140 dedicated cyclotron that meet the requirements of all main directions of applied research at FLNR.

In years 2017-2021 the equipment park was significantly augmented with modern analytical methods, including high-resolution transmission electron microscopy (Talos F200i), energy dispersive and crystal diffraction X-ray spectroscopy, differential scanning calorimetry, termogravimetry, nanofiber electrospinning machine, Raman spectroscopy, and others. Ion track methodology was used in combination with new thin film, multilayer technologies, magnetron sputtering and new promising materials (grapheme, plasmonic materials).

The results of the works performed under the auspices of the program were published in more than 120 scientific papers, mostly in international journals with high ratings, for example, Nature Communications, Journal of Nuclear Materials, Journal of Applied Physics, Small, Nanoscale, Carbon, Nanotechnology, Journal of Membrane Science, Materials Today Chemistry, Separation and Purification Technology, and others. We paid attention to increasing the quality of publications. The diagram below shows the numbers of papers published in journals ranked Q1 and Q2 in years 2017-2021.



The undertakings carried out in the framework of program 04-5-1131-2017/2021 comprise a cycle that can be continued until the end of the JINR 7-year plan under the same title "Radiation Physics, Radiochemistry, and Nanotechnology Investigations Using Beams of Accelerated Heavy Ions."

As a consequence of the importance of this research work, as well as in order to complete the tasks foreseen in the seven-year plan of development of JINR for the years 2017-2023, proposed hereby is the prolongation of the present theme for the period of 2022-2023.

In the research work under the current program, actively involved are scientific organizations from the JINR member states and associate members - Belarus, Bulgaria, Hungary, Vietnam, Germany, Spain, China, Kazakhstan, Moldova, Mongolia, Poland, Russia, Romania, Serbia, Slovakia, the USA, Czech Republic, South Africa. Due to the interest of the participating countries in the program subjects and the results of the research, regular financial support was provided in the form of grants of the Plenipotentiaries and from targeted co-operation programs. The financing from these sources was 806.3 thousand US dollars in total.

The laboratory building of FLNR is mainly outfitted with equipment owned by the state corporation Rosnano and operated on a rent basis. Thus, the laboratory building and the equipment complex required annual funding of 500 thousand US dollars per year (see Table 1).

A significant part of the research work carried out in the framework of the proposed program was performed by staff of the self-managed unit of FLNR “Center for Applied Physics”. Correspondingly, for the work reported hereby, an additional 500 thousand US dollars per year was invested from FLNR extrabudgetary funds.

Main data on the executed program

Title: “Radiation Physics, Radiochemistry, and Nanotechnology Investigations Using Beams of Accelerated Heavy Ions.”

Time period of execution of works: **January 2017 - December 2021.**
Program leaders: S.N. Dmitriev, P.Y. Apel

Table 1. Total program costs: 3222,9 thousand US dollars.

NN	**Name of budget articles**	**2017**	**2018**	**2019**	**2020**	**2021***
1	Wages (art.1 – art.3)*	66.5	66.5	66.5	66.5	142.0
2	MNTS (art.4)	30.0	30.0	30.0	30.0	50.0
3	Materials, equipment (art.5+6+9+10+18+19)	500.0	500.0	500.0	500.0	500.0
4	Electricity/water (art.7+art.8)					
5	Operational expenses (art.11 - art.17)**					67.9
6	Administrative expenses	28.5	30.8	33.3	36.2	51.2
	TOTAL:	**625.0**	**627.3**	**629.8**	**632.7**	**708.1**

* The budget approved by the Plenipotentiary Committee on 25.03.2021.

Other sources of financing:

1. Participant countries authorized representatives’ grants and co-operation programs with participant countries (616.3 thousand US dollars for 5 years in total)
2. The JINR-RSA agreement (170.0 thousand US dollars for 5 years)
3. FLNR extrabudgetary funds – 500 thousand US dollars per year.

Selected publications:

1. R. A. Rymzhanov, N. Medvedev, J. H. O’Connell, A. Janse van Vuuren, V. A. Skuratov, and A.E. Volkov. Recrystallization as the governing mechanism of ion track formation. Sci. Rep. 9 (2019) 3837. https://doi.org/10.1038/s41598-019-40239-9.

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9. O.V. Kristavchuk, I. V. Nikiforov, V. I. Kukushkin, A. N. Nechaev, and P. Yu. Apel. Immobilization of Silver Nanoparticles Obtained by Electric Discharge Method on a Track Membrane Surface. Colloid J. 79 (2017) 637–646. DOI: 10.1134/S1061933X17050088.

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