

Vladimer Chavchanidze Institute of Cybernetics of The Georgian
Technical University

Projects received with foreign grants 2018 -2023.

Appendix 4

№	Grantor	Project Name	Project start and end years	Head of Project	Volume (Amount)	Status Finished /Current	Grant Code
1	International Science and Technology Center (ISTC)	Enhancing the thermoelectric conversion performance of cobalt-based oxide materials through doping and microstructure modulation	2022-2025	Giorgi Mumladze	199 910 USD	Current	GE-2776
2	Central European Research infrastructure Consortium CERIC-ERIC.	Investigation of the effect of pulsed arc discharges on the surface modification of biologically applicable magnetic nanoparticles	30-08-2019 - 30.08.2020	Vladimer Mikelashvili	1100 EURO	Finished	20192 124
3	Scientific Technology Center in Ukraine – STCU	Development and study of new nanomaterials for the self-regulated magnetic hyperthermia of cancer cells	23.03.2018– 22.03.2020	Archil Chirakadze	30 050 USD	Finished	7089

4	Central European Research infrastructure Consortium CERIC-ERIC	Complex study of the structure and morphology of coated superparamagnetic iron oxide nanoparticles in ferrofluids obtained by new controllable technique	20/11/2017-20/11/2019	Jano Markhulia	-	Finished	Proposal 20177 016
5	Shota Rustaveli and STCU - Ukrainian Science and Technology Center.	Development of new technologies for growing nanowires and manufacturing ultrasensitive gas sensors	01.06.2016 – 01.06. 2018	David Jishiashvili	34 950 USD	Finished	SRNSF N04/0 5- 2016, USTC #6204
6	Shota Rustaveli and STCU - Ukrainian Science and Technology Center	Planning of placement of objects and cargo transportation in extreme situations	30/06/2017-30/11/2018	G.Sirbiladze - Tbilisi State University and Giorgi Bolotashvili -Institute of Cybernetics of The Georgian Technical University	70 000 USD	Finished	STCU/ GNSF № 6297
7	International Scientific Technology Center - ISTC	Investigation into visualization of prostate cancer at early stage of development	01/03/2016-01/03/2018	Besarion Partsvania	127 700 USD	Finished	G- 2188

ABSTRACTS

1. " Enhancing the thermoelectric conversion performance of cobalt-based oxide materials through doping and microstructure modulation " (2022-2025; Head of Project -Giorgi Mumladze)

Growing demand for energy consumption and the negative environmental impacts of pollution and global warming has become a major challenge facing the world today. A large amount of the world's energy consumption (70% of total energy) is wasted in the environment as heat, which raises

global environmental issues. This has led to increased activity in developing alternative eco-friendly energy conversion technologies. The future of energy is green and renewable. Being green energy materials, thermoelectrics can generate clean energy by converting low-grade waste heat directly into profitable electrical power via the so-called Seebeck effect. The development of efficient thermoelectric (TE) materials is expected to provide a breakthrough in the widespread application of thermoelectric generators (TEGs) for electrical power generation from waste heat discharged from various systems (industrial furnaces, incinerators, automotive exhaust, etc) and heat emanating from renewable energy sources (e.g., solar and geothermal). TEGs convert the dissipated heat into electricity with zero emission of toxic gases, and without vibration; TEGs are silent, extremely reliable, and with no moving components, making them ideal for small, emission-free, and less costly power generation. So we can believe thermoelectricity as an alternative and simplest Green Technology applicable for direct heat-to-electricity conversion. State-of-the-art thermoelectric materials with promising heat-to-electricity conversion efficiency must not only possess high TE performance but also be stable at high temperatures and be composed of non-toxic and low-cost elements, which is a major criterion of today's global ecological challenge. The recent discoveries of large TE responses in $\text{Ca}_3\text{Co}_4\text{O}_9$, $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_y$, and $\text{Bi}_2\text{Ca}_2\text{Co}_{1.7}\text{O}_y$ cobaltites and other oxides gave rise to enormous interest of various research groups. The cobaltite TE materials are advantageous, exhibiting many attractive characteristics, such as (i) chemical stability and thermal durability, (ii) inexpensiveness, (iii) environmentally friendly and safe application in air. Nevertheless, due to their relatively low performance when compared with the conventional ones the practical use of cobaltites still remains a problem. Proper doping, nanostructuring, and defect engineering are promising strategies to enhance the functional properties of thermoelectric materials. Very recently our superconductivity research group at the Georgian Technical University launched the studies of thermoelectric cobaltite materials in Georgia — the first laboratory of energy-efficient technologies in Georgia and the Caucasus region was successfully established. Our latest results show that using the suitable dopants selected by the Project participants leads to the significant improving of thermoelectric efficiency in cobaltites. Based on these results, 4 patent applications were submitted to the National Intellectual Property Center of Georgia ("Sakpatenti") by the project participants. The Georgian team has long-standing experience of collaboration with Armenian colleagues. A key feature of this project is that the strengths of the Georgian and Armenian partners will be combined to address materials development and investigating their thermoelectric properties. The ambitious goal of the joint Georgian-Armenian Team is to enhance markedly the heat-to-electricity conversion efficiency of cobalt-based $\text{Ca}_3\text{Co}_4\text{O}_9$, $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_y$, and $\text{Bi}_2\text{Ca}_2\text{Co}_{1.7}\text{O}_y$ thermoelectric materials via combined routes of doping and microstructural engineering at the nanoscale. We hope that the innovative approaches of this Project will pave a promising pathway toward realizing practical applications and commercialization of thermoelectric generators for waste heat recovery, using high-performance thermoelectric materials developed by the Project Team.

2. " Investigation of the effect of pulsed arc discharges on the surface modification of biologically applicable magnetic nanoparticles" (2019-2020; Head of Project - Vladimer Mikelashvili)

In 2019, within the framework of the mentioned program, research grant #20192124 - "R: Investigation of the effect of pulsed arc discharges on the surface modification of biologically applicable magnetic nanoparticles" was implemented, the main goal of which was to develop simple, economical and reproducible synthesis and characterization methods of biological iron oxide nanoparticles obtained using electrohydraulic discharges.

For this purpose, Small-Angle X-ray Scattering (SAXS), Dynamic and electrophoretic Light Scattering (DLS, ELS) in SOMAPP (Soft Matter Application Lab) laboratory of the Graz University of Technology (Austria) Through the technique, research was carried out on the suspensions containing iron oxide nanoparticles surrounded/covered with various bioactive materials (citric acid, dextran, folic acid) synthesized by us for biological use. Studies have shown that the size of our obtained nanoparticles is in the range of 25-28 nm (confirmed by SAXS) and is stable for a long time (confirmed by DLS).

Also, based on the characterization of other additional physicochemical properties (X-ray structural analysis - XRD, Fourier transform infrared spectroscopy - FTIR, ultraviolet/visible spectroscopy - UV/Vis), it was determined that iron oxide nanoparticles obtained with such properties are suitable candidates for biological applications, such as tumor therapy, Contrast agents in magnetic resonance imaging, targeted drug delivery, immunotherapy, and hyperthermia.

3. " Development and study of new nanomaterials for the self-regulated magnetic hyperthermia of cancer cells" (2018-2020; Head of Project - Archil Chirakadze)

A vast amount of nanoparticles has been developed and proposed for the local hyperthermia of cancer during the last decades, but only a few of them correspond to the mandatory requirements of having therapeutic range Curie temperature ($T_C=41-45^{\circ}\text{C}$), high-rate crystallinity and "strong" magnetic properties, strictly controlled homogeneity and dispersion of the nanoparticles, good biocompatibility and harmless decomposition products. Among them are the nickel-copper (Ni-Cu) and silver doped lanthanum manganite ($\text{Ag}_x\text{La}_{1-x}\text{MnO}_3$) nanoparticles. The developed research showed that the materials obtained at lower than usual temperatures using microwave enhanced syntheses and annealing can be successfully used for local hyperthermia revealing high magnetic properties. Behavioral toxicity testing of the developed nanoparticles was enhanced by blood oxygen saturation measurements using noninvasive oximetry in white rats. Both of the developed nanomaterials revealed a lower toxicity level than the commercially available Fe_2O_3 nanoparticles.

4. " Complex study of the structure and morphology of coated superparamagnetic iron oxide nanoparticles in ferrofluids obtained by new controllable technique" (2017-2019; Head of Project - Jano Markhulia)

The synthesis of iron oxide nanoparticles, as well as the preparation and research on their basis as biocompatible magnetic nanocomposite materials with the required physicochemical characteristics, is an urgent task today. The main technological challenges of the synthesis of biomedical magnetic

nanoparticles are the precise control of size, shape, size distribution, and stability of NPs in various physiological environments.

The aim of this research was to obtain water-based nanofluids containing superparamagnetic iron oxide nanoparticles (SPIONs) modified with various organic molecules (citric acid (CA), folic acid (Fa), oleic acid (OA), and poly(ethylene glycol) monooleate (PEGMO) with molecular weights of 460 and 860) using a modified controlled chemical coprecipitation reaction (in an automated chemical reactor with the choice of optimal synthesis conditions), as well as stable nanofluids containing bare iron oxide nanoparticles (BIONs) in an aqueous medium at normal pH (close to physiological) and study their physical-chemical characteristics. Individual samples (such as citric acid and folic acid-stabilized magnetic fluids (CA-SPIONs, FA-SPIONs)) of the obtained magnetic nanofluid were processed by electro-hydraulic discharge to improve homogeneity as well as sorption properties.

In order to achieve the goals set within the framework of the research work, a complex analysis of the synthesized samples was carried out using modern scientific research techniques. In particular, to determine the size, size distribution, sedimentation, and aggregate stability of iron oxide nanoparticles, research techniques such as small-angle X-ray scattering (SAXS) (SAXSPoint 2.0, Anton Paar), small-angle neutron scattering (SANS) (SANS diffractometer Yellow Submarine, Budapest), dynamic light scattering (DLS), and electrophoretic light scattering (ELS) (Litesizer 500, Anton Paar) were used.

Within the framework of the project, the above-mentioned samples were synthesized in the nanocomposites laboratory at the Vladimer Chavchanidze Institute of Cybernetics of Georgian Technical University. According to the project plan, measurements were made by SAXS and DLS at the Institute of Inorganic Chemistry, Graz University of Technology, soft matter application lab (Graz, Austria), while SANS measurements were performed at the Budapest Neutron Centre (Budapest, Hungary).

In this study, we have successfully synthesized magnetic nanofluids based on magnetite nanoparticles, both without modification (BIONs) and modified with oleic acid, citric acid, folic acid, and PEG monooleate, by modifying the standard procedure for coprecipitation synthesis in an automated chemical reactor. This path (with the established optimal parameters) is an easy, reproducible, scalable, and effective strategy for obtaining functionalized magnetic nanoparticles, wherein the obtained water-based magnetic nanofluids (close to physiological pH) containing naked magnetite nanoparticles retain sedimentation stability due to electrostatic stabilization. Such magnetic nanofluids can be used for biomedical purposes where high magnetization is required at a neutral or physiological pH of an aqueous medium. Due to their good solubility in water, biocompatibility, and the presence of functional groups, the obtained magnetic nanofluids modified with biocompatible organic molecules such as citric acid, oleic acid, and folic acid, as well as PEG derivatives (PEGMO), can be additionally functionalized with biomolecules or drugs, which gives promising prospects for their application in biomedicine.

As a result of processing and analysis of experimental data (as well as based on physical measurements performed using other research methods), two scientific articles were written and published (see References [1], [2]; as well as participated in a scientific conference –NANOTECH / BIOTECH FRANCE 2021.

5. " Development of new technologies for growing nanowires and manufacturing ultrasensitive gas sensors" (2016-2018; Head of Project - David Jishiashvili)

The first objective of this Project was the development of pyrolytic technology for the growth of one dimensional (1D) nanomaterials using the active ambient produced after pyrolytic decomposition of hydrazine (N_2H_4) and Ammonium chloride (NH_4Cl). Besides, the development of a microwave-assisted technology for the growth of nanowires. The second goal was the application of grown nanowires for the fabrication of gas sensors with the sensitivities in the range of several ppm-hundreds of ppb.

Two technological vacuum systems were constructed. The both used the vertical quartz reactor, but the first has a glass system, while the second was built using metal vacuum system and polypropylene vacuum pipe system. The ampoule with hydrazine was attached to the reactor, which was providing it with a hydrazine vapor having the saturated pressure (10 Torr at room temperature and higher at elevated temperatures. The source materials (Ge, InP, Ga, In, Zn etc,) were placed on the bottom of a reactor and heated from the bottom by a resistive furnace up to $700^\circ C$. It was established that NH and NH_2 radicals play an important role in producing the nitrides and reduction of surface oxides, The water molecules, presented in hydrazine with the concentration of 3 mol.%, were forming the volatile suboxides like GeO, In_2O , Ga_2O , which were performing the mass transfer of source materials to the substrate and after chemical reactions they were producing the 1D nanostructures on the substrate surface.

Using this technology following nanowires were produced: Ge_3N_4 , InP, In_2O_3 , InN and InN decorated $In_2Ge_2O_7$. Besides the InP/ Ga_2O_3 and InP/ $Zn_3(PO_4)_2$ core shell nanowires were synthesized. The theoretical study and modelling of nanowire growth process and chemical reactions for the growth of nanowires were performed. It was found that in hydrazine vapour, containing oxidizing (H_2O) and nitriding (NH, NH_2) species, it is thermodynamically preferable to synthesize the Ge_3N_4 then GeO_2 when Ge source was used. In contrast to this, when In source was annealed in the same ambient, it was preferable to produce the indium oxide, instead of InN.

The gas sensor test chamber was constructed and used for the analysis of sensors, fabricated on nanowire networks, grown by the developed technology. For producing the gas sensors we used the interdigitated gold electrodes with 5 mcm spacing, formed on the Pyrex glass surface (the electrodes were supplied by Spanish Firm "Micrux Technologies"). The nanowires were dissolved in a drop of ethanol and drop-drayed on interdigitated electrodes. The measurements were performed using computer controlled stage and Keithley-2400 source meter with the sensitivity of tens of picoamperes. Following parameters of gas sensors were evaluated: detection limits, sensitivity and its temperature dependence, response - recovery and dynamic characteristics, repetitive response.

The best results for ammonia sensing were achieved when In_2O_3 nanowires were used. The detection limit for this sensor was 0.7 ppm at $280^\circ C$, with the mean response and recovery times of 30 and 11 seconds. InN decorated $In_2Ge_2O_7$ nanowire-based gas sensor showed the best detection limit of

40 ppm when sensing methane. The mean values of response -recovery times were 45 and 51 seconds. These characteristics are close to those, reported in the literature for the best gas sensors.

6. " Planning of placement of objects and cargo transportation in extreme situations" (2017-2018; Head of Project - G.Sirbiladze - Tbilisi State University and main researcher Giorgi Bolotashvili -Institute of Cybernetics of The Georgian Technical University)

The project aims to create an expert knowledge-based intelligent support system for the private or state organizations, which are interested in extreme and abnormal processes and provide optimal and safe management of supply needed for the civil and military objects in geographical areas, affected by disasters, earthquakes, fires and other accidents, weapons of mass destruction, terrorist attacks, etc.; for the organizations, which ensures quick assistance to the population in a safe way, recovery and location of information and telecommunications networks.

As an alternative to the classical modeling, we create new approach - fuzzy facility location/transportation problem for extreme environment, in which we develop fuzzy methods and aggregations for formation and representing expert knowledge, which is the basis for the construction of high-value and high-credible intelligent technologies.

The main product of the project will be intelligent support system for the distribution networks and emergency managers.

7. " Investigation into visualization of prostate cancer at early stage of development" (2016-2018; Head of Project - Besarion Partsvania)

Objective of the project was development and fabrication of working prototype of device for prostate cancer visualization. Scope of project work was prostate cancer diagnosis. Technical approach was based on investigation of possibility penetration of the biological tissues and particularly prostate tissue by the infrared radiation. For this purpose we used different sources of infrared radiation such as light emitted diodes (LEDs) and Lasers emitting infrared radiation. Wavelength interval of irradiation was 810-890 nm. For obtaining optimal irradiation different irradiation powers were examined. Detection of irradiated infrared light was performed using CCD matrix. We examined matrixes with different resolutions and sensitiveness. For obtaining of infrared image between infrared light source and CCD matrix isolated prostate was placed.

Working model of device for prostate cancer visualization and diagnosis at early stage of tumor development is developed and created. Operation principle of device is based on the penetration ability of near infrared radiation into biological tissues and particularly into prostate tissues.. CCD camera converts infrared radiation passed through a prostate into electrical signals. These signals are accepted by PC. Developed software converts this information into visible images. The infrared radiation source is developed for prostate illumination.

It is shown that prostate tissue is transparent for infrared radiation and maximum penetration of this radiation is observed on 840-860 nm wavelengths interval.

- transmissivity to infrared radiation of the prostate noncancerous tissue is much higher than transmissivity for cancerous tissue.
- Intensity of infrared radiation passed through the prostate tissue linearly depends on tissue thickness of healthy prostates.
- Intensity of infrared radiation passed through the prostate tissue depends highly non-linearly on tissue thickness of cancerous prostates.
- Areas corresponding to the cancerous outgrowths are characterized by high optical density.
- Optical density of areas corresponding to cancerous outgrowths in the infrared image depends on cancer aggressiveness. As higher is aggressiveness as higher is optical density.
- Developed software measures different parameters of infrared images and recognizes cancerous outgrowth with 95% probability. Software gives opportunity to detect cancerous outgrowths as small as 5 mm.