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Lectures

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Mathematical Modelling of the Properties of Soft Magnetoactive Materials

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The insertion of magnetic nanoparticles into liquid or elastic matrices, into biological fluids and tissues, makes it possible to obtain new functional materials that combine the mechanical properties of a liquid/elastic matrix with the ability to perceptibly interact with a magnetic field. The basis of high-tech or biomedical application of such soft magnetoactive composites is the ability to control their rheological, magnetic, elastic, optical thermal properties by an external magnetic field. Predicting the behavior of these materials requires the development of mathematical modeling methods that take into account the specifics of structural units and the "rules of life" of large groups of these objects. The study discusses the methods and approaches used in mathematical modeling of the equilibrium and dynamic properties of statistical ensembles of magnetic nanoparticles. Special attention will be paid to the consideration of the interparticle dipole-dipole interaction, that makes it possible to apply the results of mathematical modeling to describe the properties of sufficiently concentrated systems which are sensitive to the action of even weak magnetic fields, and therefore the most interesting for applications.

Modelling Transport of Magnetic Complex Colloids

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Nano- or micro-fluidics are undoubtedly highly challenging parts of hydrodynamics, as the concept of representative volumes breaks and the thermal fluctuations matter as much as the interactions. The idea of creating magnetically controllable colloids whose rheological properties can be finely tuned on the nano- or micro-scale has caused a lot of experimental and theoretical effort. The latter resulted in systems whose building blocks are ranging between single magnetic nanoparticles to complexes of such nanoparticles bound together by various mechanisms. The binding can be either chemical or physical, reversible or not.

Systems we would talk about are different in size, shape and rigidity: they range from 20 nm to several micrometers; they can be spherical, cubic, soft or hard; those particles can be exclusively made of magnetic material or based on a polymer matrix. Among those systems are cobalt-ferrite nanocubes that are able to self-propel, polymer-like chains made of DNA cubes and nanogels. The model representations of the latter can be found in Fig. 1.

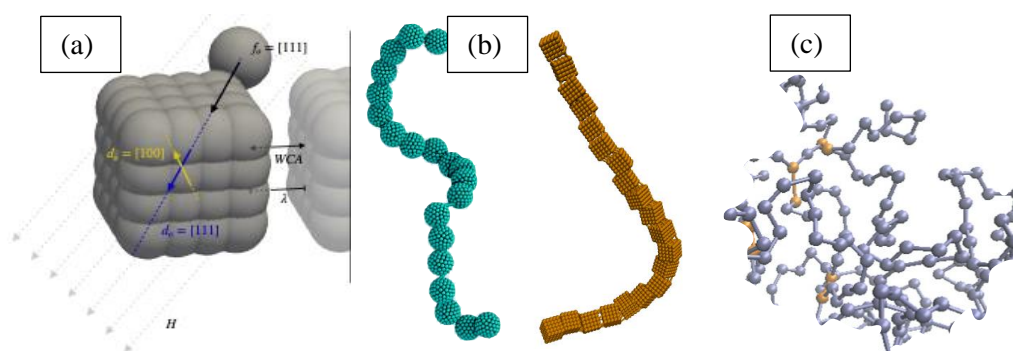


Figure 1. Magnetic active cube (a); Polymer-like structures (b); Nanogel (c).

We employ Molecular Dynamics computer simulations coupled with explicit solvent modelled by Lattice-Boltzmann approach [1,2] in order to model the behaviour of the systems mentioned above, aiming at deeper understanding of the key interactions, control parameters and magnetic response [3,4,5,6].

In my lecture I would walk you through the basic steps, one needs to make, in order to efficiently use computer simulations for investigating the rheology of nanoscale systems.

- [1] F. Weik et al, EPJ Special Topics 227, 1789 (2019).
- [2] B. Dünweg and A.J. Ladd, Advanced Computer Simulation Approaches for Soft Matter Sciences III, Advances in Polymer Science, Springer Berlin Heidelberg (2008).
- [3] I. Novikau I. et al, J. Mol. Liq. 346, 118056 (2022).
- [4] M. Kaiser and S. Kantorovich, J. Mol. Liq. 360, 119318 (2022).
- [5] D. Mostarac et al., Nanoscale (2022).
- [6] D. Mostarac and S. Kantorovich, Macromolecules (2022).

Fluoropolymers – unique materials for unique applications

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According to the apt expression of one of the leading Soviet scientists involved in the chemistry of fluorine and its compounds, Academician I.L. Knunyants - "Ftoroplasts are materials that have an eagle's heart in the skin of a rhinoceros." This means that fluorinated polymers can be used in various fields of science and technology as functional materials with unique characteristics such as superhydrophobicity, proton conductivity, piezoelectric and ferroelectric properties, and the shape memory effect. At the same time, thanks to the fluorocarbon frame, products made of fluoroplastics can be used in harsh conditions of aggressive environments and elevated temperatures. In addition, fluorine-containing polymers are highly bioinert, which makes them widely used in biomedical applications.

This paper considers various examples of the use of fluorine-containing polymers and composites based on them as smart materials.

Piezoelectric materials based on polymers, such as polyvinylidene fluoride (PVDF) or its copolymer with trifluoroethylene, have a number of unique advantages over inorganic materials, such as good mechanical flexibility, ease of molding, chemical stability, and biocompatibility [1]. They are used as indestructible control sensors in aircraft and automotive industries, space technology, that is, in those areas of technology where extreme operating conditions are present. In biomedical applications, in its piezoelectric form, PVDF can be used to develop sensors and actuators, including artificial muscles [2] and smart skin [3].

Fluoropolymers are widely used as ion-exchange materials used as membranes in various electrochemical devices, such as electrolyzers for the production of chlorine, hydrogen, and alkali [4], low-temperature fuel cells [5], and sensor systems [6].

Grafting various so-called "soft" segments, such as polyethylene glycol methacrylate methyl ether, onto the fluoropolymer backbone makes it possible to obtain materials with a shape memory effect. In [7], the melting temperature of soft segments was brought to the temperature of the human body (35.3–40.9°C), which made it possible to use these materials in biomedical applications.

[1] R.A. Surmenev, Nano Energy 79 (2021).

[2] C.S. Haines, Proc. Natl. Acad. Sci. USA 113 (2016).

[3] X.L. Qiu, Appl. Phys. 108 (2010).

[4] Y. Tanaka, Ion exchange membranes (2nd ed.) Ch. 19 (2015).

[5] L. A. Vielstich (Eds), Handbook of Fuel Cells: Fundamentals, Technology and Applications (2003).

[6] S. Hassan, Sens. Actuators B. 208 (2015).

[7] G. A.Eken, European Polymer Journal 114 (2019).

Magnetoactive Elastomers Based on Bottlebrush Polymers

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Magnetoactive elastomers (MAEs) comprising soft elastomer matrices filled with microsized magnetic particles belong to a class of smart materials due to their ability to change a number of physical properties when an external magnetic field is applied [1,2]. Among the most prominent effects observed in these composites are giant magnetorheological and magnetodeformational effects [1,2]. MAEs are receiving a lot of attention nowadays demonstrating a high potential in various industrial and biomedical applications [3,4].

In this presentation, a short review of the effects of MAE synthesis and composition on their magnetic response is presented. Then, the results of our recent development of new dispersing media for magneto-polymer composites are shown. The main focus is on MAEs based on molecular bottlebrushes, i.e. macromolecules with densely grafted side chains. The bottlebrush architecture of polymer network strands allows to finely tune the MAE mechanical properties in a broad range by changing the length and grafting density of side chains as well as the length of the main chain. Furthermore, the side chains effectively dilute the system reducing its modulus, and thus enhancing its magnetic response, without using any low-molecular-mass plasticizer. The deformation response of the material even without any magnetic field is strongly affected by the concentration of magnetic particles, so that the particle-filled bottlebrush elastomers demonstrate concurrent enhancement of both modulus and firmness, which allows mimicking the stress-strain response of assorted skin tissues [5]. In the presence of a magnetic field, bottlebrush MAEs demonstrate three orders of magnitude increase of the elastic modulus accompanied by almost 10-fold decrease of the damping factor. Using uncross-linked copolymer bottlebrushes with a small fraction of segregating side chains one can produce materials with a huge magneto-temperature response. Thus, molecular controlled dispersing media allows one to create magnetoactive materials not only with improved properties, but also with a new range of functionality.

[1] M. Shamonin and E. Y. Kramarenko, Highly responsive magnetoactive elastomers. In: *Novel Magnetic Nanostructures*, Elsevier, 2018, pp. 221–245.

[2] E.Yu. Kramarenko, G.V. Stepanov, A.R. Khokhlov. *INEOS OPEN*, 2 (6), 178 (2019).

[3] Y. Li, J. Li, J.; W. Li, H. Du. *Smart Mater. Struct.* 23, 123001 (2014).

[4] Iu. Alekhina, E. Kramarenko, L. Makarova, N. Perov. In: *Magnetic Materials and Technologies for Medical Applications*. Ed.A.M. Tishin, Elsevier Ltd., 2021, pp. 501-526.

[5] S.A. Kostrov, E. Dashtimoghadam, A.N. Keith, S.S. Sheiko, E.Yu. Kramarenko. *ACS Appl. Mater. Interfaces*, 13, 38783 (2021).

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Magnetic elastomer: rheology and magnetism for biomedicine and energy transformation applications

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Magnetic elastomers, or magnetorheological elastomers (MRE), represent the polymer media with embedded ferro- (ferri-) magnetic particles. The simple description hides the unique properties and wide range of application of MRE. New additive technologies of manufacturing of MRE allow to produce architected materials with tailor-made properties and functionalities. At the same time, the problem of investigation of magnetic elastomers as well as the problem of its “intelligence” are still opened. Why the polymer with ferromagnetic particles become “smart”? Is it “smarter” than piezoelectric materials or high-relevance multiferroic layered structures?

The fundamental principles of interaction between FM particles in elastic medium, the possibility to modern MRE will be discussed. For instance, the magnetic hysteresis loop of multidomain ferromagnetic materials should be compared with the loop of MRE based on ferromagnetic nanoparticles. They should reveal superparamagnetic behavior, but their interactions and elastic links lead to another properties. Such principles are important for applications of MRE in biomedicine and soft robotic directions. MRE can be used as a smart biomaterial for tuning the cell mechanobiology, e.g., tissue engineering (which aims to regenerate tissue more efficiently) [1]. The remote control of MRE by external magnetic field, the biocompatibility of polymer, the heating of magnetic particles and their conductivity or non-conductivity are the advantages of MRE. All these properties directly depend on the type of magnetic particles, their shape and concentration, on the elasticity and viscosity of polymer matrix, etc.

Further, the interaction can be indirectly influenced by non-magnetic particles. The addition of ferroelectric particles changes the interaction between magnetic sub-phases, that was confirmed by interesting and comparatively novel FORC-analysis method. Moreover, the application of an external electrical field to MRE with ferromagnetic and ferroelectric particles leads to the changes of its magnetic properties, thereby the material can be classified as multiferroic. Multiferroic materials are widely used in modern electronic devices, in the systems like “smart house”, etc. Some of experimental studies confirmed the magnetoelectric effect in polymer-based elastomer, and numerical experiment showed the contribution of elastic mutual influence of two types of particles on each other [2].

Bending properties of MRE resulted in development of new type of layered structure, where one of the layer was piezopolymer and the second layer – magnetic elastomer. That is another example of the fact, that investigation of magnetic elastomers covers completely different and interesting problems of modern fundamental and applied science, part of them will be presented.

[1] E. Yarali et al., Applied Materials Today 75, 101306 (2022).

[2] L. A. Makarova et al., Polymers 14, 153 (2022).

Smart textiles based on polymer composites for technical and medical applications

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Over the past 20 years, scientists have developed many different approaches and concepts for creating conductive materials that have received partial commercial application. Today, when creating electrically conductive products, engineers can choose from organic polymers, semiconductors, and metal-based materials. Depending on the production scheme, the electrically conductive element can be used during the production of textiles, for example, in the form of electrically conductive yarn or metal wire, or applied at a later stage, for example, in the form of prints with electrically conductive paints or embroidery elements. This allows IEDs to be deeply integrated into textiles through a combination of different technologies and materials. As a result, important fabric characteristics such as flexibility and elasticity can be maintained. The creation of affordable electrically conductive threads can be seen as a first and highly relevant step for the future production of smart fabrics for a wide range of technical and medical applications.

- miniaturization of conductive elements to the size of threads;
- formation of flexible conductive structures;
- reduction of energy consumption;
- wireless communication and data reading.

One of the ways to obtain conductive threads, which can be promising in the development of smart textiles, is the creation of composites based on fiber-forming polymers (PP, PA, PET, PLA, etc.). In general, the structure of a polymer composite material can be represented as consisting of one continuous polymer phase (matrix) and one or more dispersed phases (filler) distributed in a certain way in the matrix. Thus, the principle of obtaining fiber-forming composite yarns is to create a predetermined combination of two different phases (filler and matrix) using certain technological methods. The electrical conductivity of polymer composite materials is mainly determined by the electrical properties of the fillers, their dispersion, the structure of the polymer, and the method of introducing fillers into the polymer [2].

In this work, laboratory samples of polymer composite monofilaments with a filler from a mixture of various allotropic forms of carbon were made. The samples were obtained by the melt method using a DSM Xplore laboratory micromixer and then subjected to high-temperature orientational draw. It was found that a mixture of carbon nanoparticles of various allotropic shapes makes it possible not only to increase the electrical conductivity of a polymer composite monofilaments compared to a single filler, but also to achieve a high conductivity level and maintain the electrical conductivity of the system in the process of orientational draw by increasing the likelihood of the formation of conductive contacts between the dispersed spherical and anisometric fillers. It has been established that the obtained samples of conductive threads are resistant to UV radiation, dynamic mechanical loads and multiple heating-cooling mode.

[1] I. Khan., K. Saeed, Arab. J. Chem, 12, 908 (2019).

[2] O.A. Moskalyuk, A.N. Aleshin, E.S. Tsobkallo, A.V. Krestinin, V.E. Yudin, Physics of the Solid State, 54. 2122 (2012).

Magnetic field sensors for biomedical applications

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Latest advances of biomedical magnetic field sensors fabrication have led to their ubiquitous application in the fields of magnetocardiography, magnetotomography, magnetomyography and magnetoneurography. Despite obvious disadvantages like special magnetic shielding requirements and low resolution of devices without cryogenic cooling, magnetic field sensors are less invasive, reference free and not dependent on the dielectric properties of biological systems. Due to the progress of nano- and micro-fabrication techniques miniaturized magnetic field sensors can be effectively used in the emerging field of point-of-care devices. Point-of-care technologies are generally associated with lab-on-a-chip systems where some of the functions rely on the use and detection of functionalized magnetic nanoparticles [2]. For example, capture, preconcentration, and separation of analytes bonded with the specifically functionalized surface of the particles? mixing of lateral flows or creation of contrast in magnetic susceptibility of the biological medium for future sensing. Such features open doors for completely new applications as well as for the significant improvement of existing biomedical diagnostics methods. This work is a brief review of emerging and well-established magnetic field sensing technologies used for biomedical applications. Types of discussed magnetic field sensors include direct current superconducting quantum interference devices, search coil, fluxgate, magnetoelectric, giant magneto-impedance, anisotropic/giant/tunneling magnetoresistance, optically pumped, cavity optomechanical, Hall effect, magnetoelastic, spin wave interferometry, and those based on the behavior of nitrogen-vacancy centers in the atomic lattice of diamond.

[1] D. J. Mapps, *Sensors and Actuators A: Physical*, 106(1-3), 321-325 (2003).

[2] L. Gloag, *Advanced Materials* 31(48), 1904385 (2019).

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Magnetomechanical effects in amorphous ferromagnets and application in smart-composites with sensing functionalities

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Heat treatments of amorphous ferromagnets make it possible to realize useful combinations of induced anisotropy and magnetostriction due to interplay of different processes occurring during annealing: structural relaxation, atomic pair ordering, atomic rearrangements and internal stress relief. This results in mechanical stress-sensitive magnetization processes and magnetoimpedance (MI), which is important for stress-sensory applications. In Co-based amorphous microwires it is possible to realize a transformation of rectangular hysteresis loops into inclined loops and vice versa under application of a tensile stress. At these conditions, the impedance vs. magnetic field plots may change shape in the presence of tensile stress which at zero field is accompanied by a huge impedance change in the range of 70-162% per 100MPa. The following properties: miniature dimensions, small coercivity, tunable magnetic structure, magnetic anisotropy, magnetostriction make the wires suitable for innovative applications, for example, for testing internal stress/strain condition of polymer composite materials. The sensing operation is based on the two fundamental effects: generation of higher frequency harmonics of the voltage pulse induced during re-magnetization and magnetoimpedance.

The Perspectives of The Polymer Based Magnetic Composites

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The prospects of applied use of polymer-based magnetic composite materials have been forcing growing interest in recent years. Such materials are very promising for systems with remote control by the magnetic field. The desire to create composites with controllable properties is supported by the requests of almost all branches of industrial production - from electrical engineering and robotics to electronics and medical equipment. The variety of possible applications is primarily determined by the multifunctionality of the properties of polymer materials.

There are examples of magnetically ordered polymers [1]. However, for pronounced ferromagnetic response and tunability of properties, magneto-polymer composites are synthesized. Magnetic polymers typically include magnetic powders such as iron oxides, cobalt, strontium or nickel ferrites, and selected matrix products include epoxy resins, polyurethanes, and polyimides and so on. Such materials have weaker magnetic properties than cast or sintered magnets, but nevertheless, they open new possibilities of flexibility and element shaping for a wide variety of applications.

In addition, specific properties of the polymer allow to gain beneficial properties for the composite structure. It is possible to implement self-healing of magnetic polymers, which can be achieved by replacing classical polymer matrices with “self-healing matrices” to obtain durable and reliable materials with damage recovering [2]. This type of materials also includes “Magnetic gels”, which are highly elastic hydrogels with a magnetic filler, which are the main category of composites with enhanced self-healing properties.

The usage of conductive and ferroelectric polymers as a carrier allows the design of composites with unique electrical and, what is of special interest, magnetoelectric properties for micro-robotics, electronics and energy conversion systems of various types [3].

[1] P.E. Brough, The synthesis of a ferromagnetic polymer. Doct. Thesis (1999).

[2] Hybrid materials Based On Magnetic Nanoparticles. Basics and applications. Edited by Kayla Dos Santos. Woodhead Publishing series on electronic and optical materials. 2021, page 720.

[3] Hu U, Lum G.Z., Mastrangeli M., Sitti M. Nature. 554 (7690), 81-85 (2018).

Magnetic nanoparticles: a must-know curriculum

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Permanent magnets with their ability to attract and repel each other and to unconditionally attract everything iron-like, are the objects quite familiar to everyone. Their well-known applications span from fridge magnets and hard disks to massive industrial equipment, let alone that our Earth is a global-size magnet itself. Add to that the magnets feel each other at a distance, in other words, interact remotely. It is an everyday miracle, although we normally ignore it just because it is too customary. However, there is a big difference between a habit and understanding.

In fact, everything about permanent magnets is nontrivial and even mysterious. As the great physicists of XIX century had shown, every electric current generates a magnetic field around itself. For a closed current this is described by a vector called *magnetic moment*. The magnetic moments interact via the fields they create. A permanent magnet (ferromagnet), thus, is a collection of some microscopic currents (electron spins, in fact) whose magnetic moments are orientationally coherent.

The physics of that correlation and its stability was enigmatic until quantum mechanics appeared and introduced the *exchange interaction* that is really responsible for the coherent orientation of the electron spin magnetic moments which, summing up, build up the macroscopic magnetic moment of any permanent magnet around us. Quite a wide scientific knowledge on the properties of such magnets ensuring the ability to handle them had been accumulated since by now. The major fact on magnetism of strongly correlated spin systems are: (i) of all the atomic substances, ferromagnetism is inherent only to so-called transition metals – Fe, Ni, Co – and (ii) it is a collective phenomenon needing a notable number of atoms in very close contact no difference, is it a crystal lattice or an amorphous clot.

Two conceptual questions turn up immediately. First, how many atoms are necessary to turn the sample into a ferromagnet and, second, do the properties of the smallest possible magnet completely resemble those of a massive one? The answers cannot be given in a couple of words. But one factor should be pointed out, it is of paramount importance at the nanoscale – it is temperature. Being not very critical in non-overheated massive samples, in nanoparticles it (i) reduces the temperature range of the ferromagnetic state, (ii) strongly endangers the permanence of the magnetic moment, (iii) makes spatially free nanoparticles to move and rotate intensely in the absence of any external fields and flows.

Meanwhile, when developing smart materials – in our case one may term them *multiferroics* – these are just the nanodisperse ferromagnetic powders which are used to make a composite with a reasonably homogeneous structure. Hence, to have basic notion of the nanoparticles is a vital issue for understanding and prognosing the properties and field-responses of the would-be multi-component system. Typical fine ferroparticles employed in preparation of magneto-polymer (aka *magnetoactive*) composites are described together with their properties which predetermine their interaction with soft macromolecular matrices.

Biomimetic materials and tissue engineering

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Over the past decade, we have seen the emergence and transition to new modern trends, such as 3D and 4D printing, smart prostheses, biomimetic materials and bioprinting. High-strength endoprostheses, artificial muscles, cells for organ regeneration, patient-specific implants, bioprinting - these are just some of the developments to increase the quality of life.

Biomimetic polymer materials are widely used in different medical applications, especially as scaffolds in tissue engineering. Bone is one of the most frequently transplanted tissues. An important task is the development of so-called biomimetic scaffolds with a certain geometry and porosity, which could contribute to the differentiation of cells.

Reverse engineering approaches, which include the study of native tissue and polymer using high-resolution microscopy and CT, combined with 3D bioprinting methods, allows the formation of biomimetic anisotropic structures that repeat the architecture of cancellous bone.

Bioresorbable (PLA, PHB, PCL) and bioinert (UHMWPE and PEEK) were used as polymer base for biomimetic scaffold design. Bioceramics was used a filler to increase bioactivity of polymer matrix.

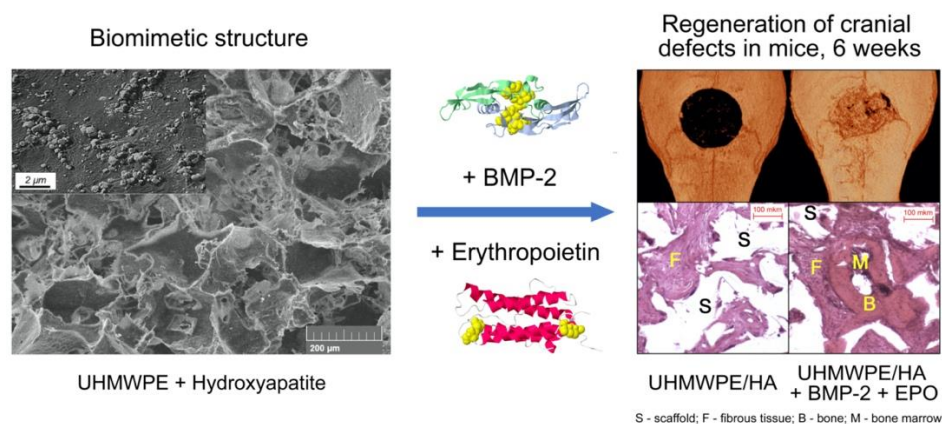


Figure 1 – Example of UHMWPE biomimetic scaffold [2]

The developed biomimetic highly porous scaffolds can be used separately or in combination with MMSC and growth factors for reconstruction of nonload-bearing parts of bones and soft tissues to solve the problems associated with difference between implant architecture and bioinertness.

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[1] F. Senatov, et al., Effect of recombinant BMP-2 and erythropoietin on osteogenic properties of biomimetic PLA/PCL/HA and PHB/HA scaffolds in critical-size cranial defects model, *Materials Science & Engineering C* (2021).

[2] Fedor Senatov, et al. Biomimetic UHMWPE/HA scaffolds with rhBMP-2 and erythropoietin for reconstructive surgery. *Materials Science and Engineering: C*, 2020, Vol. 111, 110750.

[3] Zhukova, P.A. et al. Polymer Composite Materials Based on Polylactide with a Shape Memory Effect for “Self-Fitting” Bone Implants. *Polymers* 2021, 13, 2367.

[4] Senatov, F. et al. Osseointegration evaluation of UHMWPE and PEEK-based scaffolds with BMP-2 using model of critical-size cranial defect in mice and push-out test / *Journal of the Mechanical Behavior of Biomedical Materials*, 2021, 119, 104477.

Properties of magnetic composites based on high-elastic polymers

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Classifying magnetic composite materials synthesized on the basis of high-elastic matrices as ‘smart’ is a historically developed tradition. Capable of varying their parameters under the influence of magnetic fields, they started attracting interest as recently as the 1990s as the pioneering patents emerged. Magnetoreological elastomer changing its visco-elastic properties in magnetic field was synthesized and studied at Ford Motor Company [1]. M. Zrínyi in Hungary [2] and L. Nikitin in Russia [3] investigated the phenomenon of magnetodeformation, namely the capability of a magnetic composite sample to vary its geometrical shape when influenced by a non-homogeneous magnetic field. Further research on similar materials revealed that they possess an extensive set of other specific properties including magnetostriction, magnetoresistance, magnetopiezoresistance, and exhibit the magnetodielectric, magnetoacoustic, magneto-optical, and magnetoelectrorheological effects. The material also demonstrates magnetic field-induced shape memory. At the same time, its electroconductivity is field-controllable and based on the electron-tunneling mechanism.

In this connection, such magnetic composites have various names, e.g. magnetorheological or magnetoactive elastomers and magnetic gels. The ways of their synthesis are based on the dispersing of a magnetic powder in a liquid polymer matrix followed by the polymerizing of the whole composition. Solidified under the influence of a magnetic field, the samples occur anisotropic with mechanical features depending on the direction of the tension vector. Meanwhile, an important factor is the condition of the surfaces of the particles introduced into the polymer. Preparation of a homogeneous dispersion may not be possible owing to the poor wettability and thus requires treating the powder with a surfactant. An optimal way, however, is the peptization of the disperse magnetic phase (e.g. magnetite) when after forming in the aqueous medium, it is transferred into an organic liquid with its following introduction into the elastomer semi-product to be polymerized.

All the principal effects, which magnetic elastomers exhibit, are based on reversible particles structuring taking place inside the polymer matrix.

This work was financially supported by the Russian Science Foundation (Grant No. 19-13-00340-II)

- [1] EP 0784163. Variable stiffness bushing using magnetorheological elastomers.
- [2] WO 1997002580 A1. Magnetic field sensitive polymer gels and uses there of
- [3] Pat. RF 2157013. Magnetically elastic composite material.

Soft magnetic elastomers: properties, effects and modelling

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Functional materials obtained by incorporating finely dispersed ferromagnets into polymers (elastic modulus $G \sim 10\text{--}100$ MPa) have been known for a long time. They are used to make the cores of induction coils or permanent magnets, which are less brittle than metal or ceramic. Systems in which ferromagnet microparticles are embedded in a very soft ($G \sim 1\text{--}100$ kPa) polymer matrix with a particle content of only half the maximum packing density attracted scientific and applied interest much later. These composites now form a distinct family of smart materials called magnetorheological polymers or soft magnetic elastomers (SMEs). Known examples of SME matrices are dense polymer gels (gelatin and polyvinyl alcohol) or weakly crosslinked rubbers (plasticized silicone rubbers). Micro- or nanopowders of iron or ferrites (for example, magnetite or maghemite) are used as fillers.

The difference between SME and conventional high-modulus magnetic rubbers lies in the fact that due to the fact that the magnetic and elastic interactions are of the same order of magnitude. The SME has a set of interesting properties, such as the magnetodeformation effect, the strong dependence of the elastic modulus on the field, and the shape memory effect. The magnetodeformation effect is the deformation of the sample in response to an applied magnetic field (uniform or inhomogeneous). In an inhomogeneous field, this is due to the fact that the magnetic material is affected by a panderomotor force, which pulls it into the region of a strong magnetic field. In a case of uniform field, the cause of deformation is the "desire" to reduce the demagnetizing field, which leads to elongation along the magnetic field. In response to an applied magnetic field, the SME qualitatively changes its magneto-mechanical behavior. Structuring occurs, i.e., a global network of particles that resists mechanical loading, which leads to a strong increase in the elastic modulus. Structuring also leads to a shape memory effect. In the absence of a field, such samples deform almost linearly elastically and reversibly. However, in a magnetic field, after the complete removal of the external mechanical impact, the sample retains a significant part of the accumulated deformation. It exists as long as the magnetic field remains on. After turning it off, the sample restores its original shape and properties.

SME modeling can be divided into two approaches. Indeed, being heterogeneous materials (a highly elastic matrix filled with ferromagnet microparticles), SMEs are characterized by internal multiscale and a variety of internal interactions. By modeling the behavior of a sample at the mesolevel, one can "look" inside the sample and describe the physical mechanisms that occur in a complex system, which is difficult to do in a full-scale experiment. At the macrolevel, in the continuum approximation, the thermodynamic approach with an additionally introduced structural parameter is used to obtain the SME constitutive relations.

Manufacture of magnetic nanocomposites based on PVDF and its copolymer

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Polymers due to the variety of chemical and physical, for example, elasticity, thermoplasticity and strength, as well as the structure of the molecules, can be used in various areas. In particular, the application of new polymeric materials is in demand in medicine, for example, for the creation of scaffolds and implants in regenerative medicine [1]. In this view, the use of piezoelectric polymers with unique electrical properties, such as polyvinylidene fluoride (PVDF) and its copolymers PVDF-TrFE is the most relevant today [2]. Adding magnetic filler (e.g., magnetic nanoparticles) to a piezoelectric polymer gives it magnetic properties, so when an external magnetic field is applied, such a matrix is stressed, and, due to the piezo-effect, the electrical polarization is induced [3]. Such properties can be utilized to remotely cause electrical polarization which provides new opportunities for the application of such materials.

In this lesson we will review existing methods of processing PVDF polymer [4], in order to obtain composites with the maximum possible formation of the polymer beta-phase. In this paper, the properties of PVDF polymer, its phases, as well as composites based on PVDF in the form of dense and porous films, as well as 3D fibers and spheres will be considered. The listed structures can be fabricated by various processing methods, including doctor blade, spin coating, solvent leaching of particles, solvent casting with a 3D nylon template, sublimation extraction with a 3D poly(vinyl alcohol) (PVA) template, temperature induced phase separation (TIPSPS), solvent-free phase separation (NIPSPS), and electrospinning. The structures developed by the above methods have the potential to be used in a wide range of applications, such as in the creation of sensors, as filtering materials, and in biomedicine to create neoplastics.

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Sources and literature

- [1] Saxena, P., & Shukla, P. (2021). A comprehensive review on fundamental properties and applications of poly(vinylidene fluoride) (PVDF). *Advanced Composites and Hybrid Materials*, 4(1).
- [2] O Senatov, F. S., et al. (2016). Mechanical properties and shape memory effect of 3D-printed PLA-based porous scaffolds. *Journal of the Mechanical Behavior of Biomedical Materials*, 57, 139–148.
- [3] Omelyanchik, A., et al. (2021). Boosting magnetoelectric effect in polymer-based nanocomposites. *Nanomaterials*, 11(5).
- [4] Clarisse Ribeiro, et al (2018). Electroactive poly(vinylidene fluoride)-based structures for advanced applications. *Protocol*, 13, 681–704.

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Oral Talks

Magnetoelectric composites for sensing and energy harvesting applications

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Technological evolution affects almost every aspect of our lives on the scale from everyday routine to global processes. The development of new digital technologies and robotic systems is one of the most important knowledge-intensive areas of modernization of technology and the economy. Process automation brings the need for fast and accurate signal detection as well as for the autonomy of elements power supplement. Among the sensors of various types, a huge share in terms of functionality belongs to sensors based on magnetic and magnetoelectric materials. Such sensors are used in the automotive, aviation and aerospace industries, information recording and storage systems, microelectronics, microwave absorbers and energy transformers, etc [1]. However, the progress in this field requires the investigation and design of new materials.

Among multiferroic materials layered composites are well known to have large values of magnetoelectric transformation [2]. Usually, the magnetoelectric effect in layered structures is associated with magnetostriction in ferromagnetic materials and piezoelectric effect in the ferroelectric layer. However, bending mode in flexible structures can also provide efficient magnetoelectric transformation in AC regime and, thus, good sensing capabilities for flexible electronics. Such bendable composites may be created based on magnetorheological elastomers and piezoelectric polymers.

The layered structure based on magnetorheological elastomer with iron microparticles and PVDF piezoelectric film was investigated in this work. Magnetoelectric effect in the composite occurs due to huge bending deformations of magnetorheological elastomer in gradient magnetic field. This deformation leads to corresponding bending of PVDF layer, which results in induced voltage from the sample. As a magnetoactive layer magnetorheological elastomers with various thicknesses (from 0.3 to 3 mm), iron content (40-80 wt.%), Young's moduli were used. The PVDF layer with conducting plates and protective covering was commercially available.

The experimental investigations were carried out with the measuring cell based on the microcontroller Arduino. DC or AC magnetic field was applied using electromagnet. The signal from PVDF layer was recorded during or after the interaction of multilayer with magnetic field.

The observed effect was shown to be dependent on the properties of magnetoactive layer, namely the thickness, elastic properties, and iron mass fraction in magnetorheological elastomer. It was also demonstrated that the induced voltage depended on the amplitude of the magnetic field pulse [3]. The resonant enhancement of the effect up to 300% in the AC magnetic field was also observed. The dependences obtained were explained in terms of bar oscillations under the external force.

The results of numerical simulations are in accordance with the experimental data [3].

[1] X. Hou et al., J. of Alloys and Compounds 765, 1127-1138 (2018)

[2] S.-O. Hwang et al., Integrated Ferroelectric 157, 57-62 (2014)

[3] L. A. Makarova et al., J. of Physics D – Applied Physics 54, 015003 (2020)

Gold-Arsenic sulfide nanocomposite doped porous glasses for optical applications

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Recently, broad range of applications based As_2S_3 has emerged from nonlinear application such as supercontinuum generation to passive devices such as optical fibers for the infrared region [1, 2]. As_2S_3 photonic crystal fiber reported to generate an ultra-broadband infrared supercontinuum generation extending from 2.5 to 15 μm [1]. Second harmonic generation was observed in thermally poled arsenic sulfide glasses [3]. As_2S_3 planar waveguides were used for correlated photon-pair generation and in other work for broadband cascaded four wave mixing [4]. 2D layers of As_2S_3 were shown to exhibit a highly anisotropic mechanical and optical properties. It was found that the stretchability of As_2S_3 can be even larger than graphene [5].

Photoinduced changes (PIC) of As_2S_3 is of great importance and it was widely studied in the literature [6, 7]. Several factors can influence the PIC, for example the composition $\text{As}_x\text{S}_{100-x}$, the thermal history, the preparation method, the irradiation wavelength, and the dimension of the material (bulk glass, thin films, nanolayers) [6, 7].

In our work we investigate the PIC in the optical properties and the gold nanoparticles (AuNPs) effect on this PIC of subnanolayers of arsenic sulfide doped in porous glasses (PG). To prepare the composite material a simple chemical deposition method was used. As_2S_3 powder was dissolved in amin solution and thin clean pieces of PG were impregnated in the solution for two days. After impregnation, the samples were heat treated at 190C for two hours. The solution with and without AuNPs were studied using Fourier-transform infrared spectroscopy (FTIR). Using FTIR spectroscopy it was confirmed that when mixing two solutions of arsenic sulfide and AuNPs they interact and form a complex.

The reversable PIC of the composite material were studied using Raman spectroscopy. We observed that As_2S_3 nanoparticles exhibit a reversible photo-bleaching effect (PB) which is the opposite behavior that was observed in As_2S_3 bulk glasses [6]. Introducing the AuNPs to the solution resulted in increasing the As/S composition ratio in PG.

Raman spectra showed that the impregnation of PG in As_2S_3 solution results in the formation of various As/S clusters in the pores. The addition of AuNPs to the As_2S_3 solution induces the formation of As_2S_3 clusters in the form of pyramidal structures. The formation of such clusters can be increased by subsequent treatments using irradiation and annealing.

- [1] Wei, Chen, et al. *Optik* 141 (2017): 32-38.
- [2] Shiryaev, V. S., et al. *J. Optoelectron. Adv. Mater* 16.9-10 (2014): 1020-1025.
- [3] Dussauze, Marc, et al. *Optical Materials Express* 2.1 (2012): 45-54.
- [4] Wen, Jin, and Haiwei Fu. *Modern Physics Letters B* 29.21 (2015): 1550115.
- [5] Mortazavi, Bohayra, et al. *Journal of Materials Chemistry C* 8.7 (2020): 2400-2410.
- [6] Tanaka, Ka. "Reversible photoinduced change in intermolecular distance in amorphous As_2S_3 network." *Applied Physics Letters* 26.5 (1975): 243-245.
- [7] Shpotyuk, O. I., J. Kasprczyk, and I. V. Kityk. "Mechanism of reversible photoinduced optical effects in amorphous As_2S_3 ." *Journal of non-crystalline solids* 215.2-3 (1997): 218225.

Magnetic composite filament based on polylactide PLA for 3D-5D printing

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The Fused Deposition Melting (FDM) is the simplest and commonly used method related to additive manufacturing technologies, in which a 3D object is printed from extruded layers of a thermoplastic polymer [1]. Modern trends in the development of the FDM method are in the additive printing of functional composites with various fillers [2]. One of the specific practical tasks is the additive printing of polymer composites with magnetic additives for applications in electronics, sensors, biomedicine, etc. The simplest and most affordable filament used for FDM printing is polylactide (PLA) whose monomer is lactic acid. PLA is biodegradable, biocompatible, and thermoplastic, which makes it promising for use in biomedical applications.

The main task of this work is to develop the technological approaches for the production and studies of the magnetic properties of a composite filament based on polylactide with additives of ferrite particles. The model of considered filament is a polymer composite of a cylindrical shape, consisting of polylactide (PLA), in the matrix of which magnetic particles are distributed. Three types of particles were used as additives for the manufacture of composite filament:

- nanoparticles of cobalt ferrite CoFe_2O_4 (CFO);
- a mixture of nanoparticles of pure CoFe_2O_4 (CFO) and zinc substituted $\text{Zn}_{0.25}\text{Co}_{0.75}\text{Fe}_2\text{O}_4$ (ZCFO) cobalt ferrites;
- microparticles of barium hexaferrite $\text{BaFe}_{12}\text{O}_{19}$ (BaFO).

Magnetic nanoparticles of pure CoFe_2O_4 and zinc-substituted $\text{Zn}_{0.25}\text{Co}_{0.75}\text{Fe}_2\text{O}_4$ cobalt ferrites were obtained by the sol-gel method. BaFO microparticles were obtained by mechanical grinding of a commercial pressed sample of barium hexaferrite. In first, the polymer composite consisted of magnetic particles in selected mass ratio distributed in PLA matrix were fabricated by solvent casting. Then composite were grinded to granules, which were extruded into a composite filament using commercial Twin Tech Screw 10 mm extruder at a temperature of 185 °C. The rotation speed of the extruder was 15 rpm. The extruded composite filament was cooled in air at room temperature without forced cooling. For the extrusion process, a nozzle was used, which allows the output to obtain a standard filament with a diameter of about 1.78 mm, used for FDM printing.

As a result of a series of experiments, the three samples of filament were obtained using all types of particles with a 5% wt. concentration of magnetic fillers. It was demonstrated that all three types of obtained filaments are suitable for FDM printing.

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[1] R.B. Kristiawan, F. Imaduddin, D. Ariawan, Ubaidillah, Z. Arifin, Open Eng. 11, 639–649 (2021).

[2] P.M. Angelopoulos, M. Samouhos, M. Taxiarchou, Mater. Today Proc. 37 4031–4043 (2021).

Fabrication of GRIN optical microstructures by two-photon lithography

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GRIN optics (gradient refractive index optics) is a branch of optics that deals with the propagation of light in an optically inhomogeneous medium. This article is dedicated to the two-photon lithography method for creating microstructures with GRIN.

The method is based on the phenomenon of polymerization or cross-linking of monomers with another substance, a sensitizer, a photoinitiator for example, or a photonic acid generator (**photoresist**), when radiation is absorbed - two photons with a certain energy. As a result, there is obtained a polymer. Due to the probabilistic nature of the polymerization process, it is more convenient to use radiation focusing in a small area called a voxel[1],[2]. By moving the voxel in the substance in a certain way, you can get a complete structure.

The two-photon lithography method is also suitable for creating structures with a gradient refractive index. Depending on the intensity of the radiation, more or less monomers polymerize, and, as a result, we obtain a substance with a **varying refractive index**. There are several approaches related to the preparation of the basis for lithography: 1) printing inside a porous structure made of silicon compound, can be PSi or PSiO₂, filled with photoresist [3], 2) using a thin film of photoresist [4] and others, like

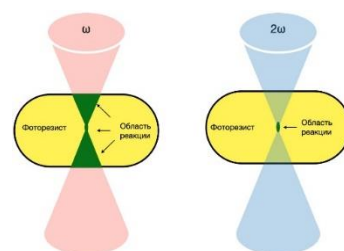


Figure 1 On the left shows the process of single-photon absorption, on the right - two-photon absorption

The purpose of my work was to improve the hardware program in order to obtain GRIN structures, and creating elementary structures for verification.

There was SZ2080 photoresist used as the basis for printing in this research. The substance was placed on a glass substrate that had undergone several stages of preparation.

A parallelepiped with a base of 25×25 microns and a height of 3 microns was chosen as the printing object. A sample of this shape was "cut" into parallel strips as it is done for 3d printers. Different parameters were used for the thickness of lines and layers, as well as for the speed and power of printing to obtain different samples. For the intensity, we chose a linear and Gaussian function depending on the coordinate in order to understand how the refractive index behaves.

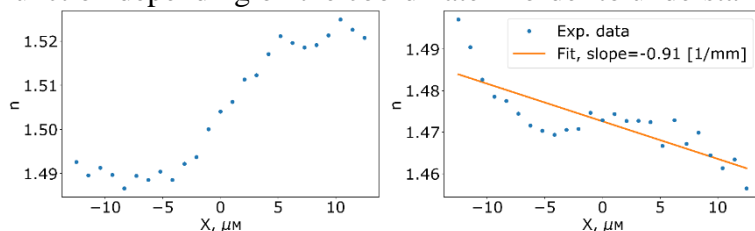


Figure 2 Graphs of the dependence of the refractive index on the X coordinate in the structure obtained for Gaussian (left) and linear dependence (right). An approximation was carried out for the linear dependence.

As a result, we obtained structures with a gradient refractive index. In the future, the method can be improved by combining a photoresist with another substance, such as magnetic particles, which will affect the passage of light through the structure.

REFERENCES

- [1] Sun, H.-B., Takada, K., Kim, M.-S., Lee, K.-S., Kawata, S. Scaling laws of voxels in two-photon photopolymerization nanofabrication // Applied Physics Letters. — 2003. — Vol. 83, no. 6. — P. 1104—1106.
- [2] Sun, H.-B., Kawata, S. Two-photon laser precision microfabrication and its applications to micro-nano devices and systems // Journal of lightwave technology. — 2003. — Vol. 21, no. 3. — P. 624.
- [3] Christian R. Ocier, Corey A. Richards, Daniel A. Bacon-Brown, Qing Ding, Raman Kumar, Tanner J. Garcia, Jorik van de Groep, Jung-Hwan Song, Austin J. Cyphersmith, Andrew Rhode, Andrea N. Perry, Alexander J. Littlefield, Jinlong Zhu, Dajie Xie, Haibo Gao, Jonah F. Messinger, Mark L. Brongersma, Kimani C. Toussaint Jr., Lynford L. Goddard and Paul V. Braun. Direct laser writing of volumetric gradient index lenses and waveguides. Light: Science & Applications (2020) 9:196.
- [4] Albertas Zukauskas, Ieva Matulaitiene, Domas Paipulas, Gediminas Niaura, Mangirdas Malinauskas, and Roaldas Gadonas. Tuning the refractive index in 3D direct laser writing lithography: towards GRIN microoptics Laser Photonics Rev. 9, No. 6, 706–712 (2015) / DOI 10.1002/lpor.201500170.

Plasma treatment of biological interfaces: effects on adhesive and mechanical properties

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Magnetoelectric polymer composites, consisting of a magnetic filler and a piezopolymer matrix, are a group of materials in which the magnetoelectric coupling is associated with strain interactions between the filler and matrix [1]. The biocompatibility of the polymer backbone and the multiferroic properties of these composites, make them interesting for various biomedical applications, for example, they can be used as biological interfaces for bone tissue engineering [2-3].

Poly(vinylidene fluoride) (PVDF) is a fluorine-containing semi-crystalline polymer derived from vinylidene fluoride, which has at least five different crystalline phases, of which the β -phase has the highest piezoelectric response. However, its hydrophobicity and low adhesion to other materials and cells due to low surface tension limits its application, including in biological applications [4]. There are many different approaches to modify the PVDF surface, however, cold plasma treatment is the most optimal method as it preserves the basic physico-chemical bulk properties of the polymer substrates and improves their adhesive properties [5].

The main objective of this work was to investigate the effect of plasma treatment on the morpho-mechanical and adhesive properties of biological interfaces. The nanocomposites were fabricated using the doctor blade method and then modified with cold plasma. PVDF modified with a magnetic filler (CoFe_2O_4) was used as the substrate. The morpho-mechanical properties of the nanocomposites were investigated before and after plasma treatment by atomic force microscopy (AFM). The nanocomposites were additionally tested on human mesenchymal stem cell culture to evaluate their adhesive properties.

This study showed how cold plasma treatment affects the morpho-mechanical and adhesive properties of nanocomposites. It was demonstrated that plasma treatment reduces the mechanical properties, increases roughness, and improves the adhesive properties of the PVDF-based biological interfaces, making them promising for use in bone tissue engineering.

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- [1] P. Martins, S. Lanceros-M'endez, Polymer-based Magnetoelectric Materials, *Adv. Funct.Mater.*, vol. 23, 3371–3385 (2013)
- [2] C. Ribeiro, V. Sencadas, D.M. Correia et. al, Piezoelectric polymers as biomaterials for tissue engineering applications, *Colloids Surfaces B Biointerfaces*, vol. 136, pp. 46-55 (2015)
- [3] A.E. Stanton et al., Extracellular matrix type modulates mechanotransduction of stem cells, *Acta Biomater*, vol. 96, 310-320 (2019)
- [4] M. Tavakoli, Surface modification of polymers to enhance biocompatibility, *Surfaces and Interfaces for Biomaterials*, Pages 719-744 (2005)
- [5] D.M. Correia et al., Surface wettability modification of poly(vinylidene fluoride) and copolymer films and membranes by plasma treatment, *Polymer*, vol. 169, 138-147 (2019).

Optical properties of carbon dots covalently bonded with metal nanoparticles

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Modification of carbon dots (CDs) is an interesting field of research since it allows control their properties in a wide range. Carbodiimide chemistry is a universal tool that can be used to bond the CDs with different nanoparticles such as metal nanoparticles (MNPs). The interaction between nanoparticles can lead to several useful effects, for instance, increased quantum yields and decreased lifetimes.

CDs were synthesized by the solvothermal method from o-phenylenediamine and benzoic acid according to the procedure adopted from [1]. Gold NPs (AuNPs) and silver NPs (AgNPs) stabilized by cysteamine were synthesized according to the procedure reported in [2] and [3], respectively.

Optical properties of CDs, AuNPs, and AgNPs are shown in Figure 1a. The MNPs were chosen to appropiate two enhancement regimes: plasmon peak is in resonance with (i) CDs absorption band or (ii) both CDs absorption and PL bands.

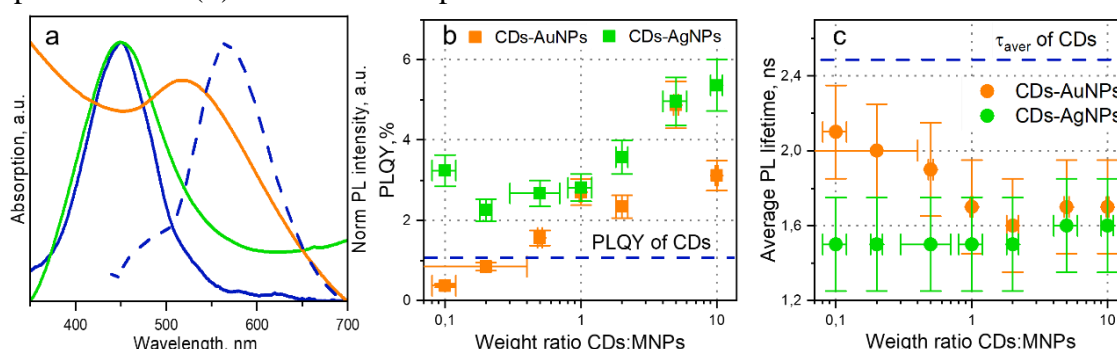


Figure 1. (a) Absorption spectra of CDs (blue), AgNPs (green), and AuNPs (orange) versus PL spectrum of CDs excited at 405 nm (blue dashed). QY (b) and average PL lifetime (c) versus weight ratio of CDs to MNP of CD-AgNP and CD-AuNP complexes. In (b) and (c), the values of QY and lifetime measured for pristine CDs are shown by blue dashed lines.

To estimate the PL enhancement depending on CDs to MNPs weight ratio, the PL quantum yield (QY) was calculated (Figure 1b). For all CDs-AgNPs complexes, the PLQY is larger than that of the pristine CDs sample (PLQY=1%). The highest PL enhancement of 5.4 was achieved at the size of CD-AgNP complexes corresponding to the formation of stable colloid. A drop of PLQY for complexes with AgNPs can be attributed to the interaction of CDs within aggregates in complexes.

For CD-AuNP complexes, at low CDs to MNPs weight ratios the PL is quenched by effective energy transfer from CDs to AuNPs because the PL band overlaps with the absorption band of AuNPs. For CD-AuNP complexes, PL enhancement is observed with maximum PLQY of 4.9 at CDs/MNPs=5. The PL lifetime of all CDs-MNPs complexes (Figure 1c) is shorter than that for pristine CDs (2.5 ns) which indicates on the increased radiative rate of CDs' charge carriers relaxation in the presence of MNPs.

[1] S. Lin, RSC Adv. 7,66 (2017).

[2] X. Liu, Colloids Surf. B, 58, 1 (2007).

[3] J. M. Oliva, Adv. Nat. Sci.: Nanosci. Nanotechnol., 9, 1 (2017).

Multi-component platform for structured RNA and double-stranded DNA detection

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The current COVID-19 pandemic has indicated a high need for fast, affordable and user-friendly diagnostic tests applicable at the point of care or at home. Such diagnostics should require a minimum number of steps and equipment. Diagnostics based on nucleic acid amplification, including PCR or isothermal amplification methods, is the gold standard for molecular diagnostics [1]. It is well known that hybridization probes are often required to detect the presence of certain nucleic acids. However, the formation of a complex between the probe and the long (>50 nucleotides (nt)) ssDNA or RNA of the analyte is complicated by the secondary and tertiary structure of the analyte [2].

Effectual point-of-care molecular diagnostic technique can be design using highly selective hybridization probes that produce visual outputs. Moreover, recognition of long folded single stranded (ss) RNA or DNA analytes should preferably be done at ambient temperatures to avoid the need for a thermostat. We propose to solve the problem of folded analyte recognition by designing multicomponent probes that can unwind secondary structures of nucleic acids. In this study, we develop general principles for constructing such probes.

Listeria monocytogenes and *Cytomegalovirus* are pathogens responsible for a number of human diseases, such as listeriosis, acute respiratory viral infections, inflammation of various internal organs, pneumonia and bronchitis. For an identification of these organisms we chose specific genes that are constitutively expressed and organism-specific ssRNA amplicons 88-87 nucleotide long were obtained in the nucleic acid sequence-based amplification (NASBA) reaction, which produces ssRNA amplicons. NASBA amplicons were analyzed by multicomponent peroxidase-like deoxyribozyme (PxDm) probes. In this approach, the probes use 1-3 analyte binding arms are designed to tightly bind and unwind ssRNA analytes, while another RNA-binding arm selectively recognized a specific analyte sequence and forms a G-quadruplex structure (G-4). The G-4 structure changes the color in the presence of hemin, H₂O₂ and a colorless organic substrate e.g diaminobenzidine. In this study, we determined lengths and fragments of ssRNA amplicon for binding by the PxDm probes arms to ensure high selectivity and high signal/background ratios (S/B).

Both *Listeria monocytogenes* and *Cytomegalovirus* NASBA amplicons were recognized with high selectivity and S/B of ~ 3, 36 without the need for isolation of RNA from NASBA reaction mixture. Surprisingly, the same PxDm is able to detect dsDNA amplicons at room temperature (shown for *Listeria monocytogenes*).

[1] M. Drancourt, A. Michel-Lepage, S. Boyer and D. Raoult, Am. Soc. Microbiol., 29, 429-447, (2016).

[2] C. Nguyen, J. Grimes, Y. V. Gerasimova and D. M. Kolpashchikov, Chem. Eur. J., 17, 1, (2017).

Obtaining and research of the properties of magneticluminescent hybrid structures based on iron oxide (Fe₃O₄) with semiconductor shells

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The use of magnetic nanoparticles and quantum dots to create a bifunctional system could expand the biomedical applications of these two functional materials and improve their current applications. Recent studies in these areas have shown that the integrated magneto-optical properties allow nanocomposites to expand their applications in biotechnology and medicine, in particular, targeted drug delivery, magnetic resonance imaging (MRI), diagnostics, bioseparation, magnetic hyperthermia, magnetic storage media, etc., such structures are also promising material for theranostics. In this work, hybrid magnetic-luminescent nanomaterials based on a core of superparamagnetic iron oxide (Fe₃O₄) with luminescent shells of zinc sulfide and zinc selenide (ZnS, ZnSe) were synthesized and studied.

In a two-in-one system of bimodal magnetic fluorescent nanocomposite materials that combine both magnetic and fluorescent properties, the key factor is the successful binding of magnetic and fluorescent materials and the prevention of luminescence quenching. The photoluminescence of such nanocomposites is complex, since it is sensitive to the conditions of synthesis and the size and shape of crystals. Iron oxide is a strong luminescence quencher and can quench the emission of quantum dots. The report will discuss the properties of quantum dots, the features of their synthesis and modification, as well as the advantages and disadvantages. This paper describes the high-temperature TOPO-TOP synthesis (trioctylphosphine oxidetrioctylphosphine) [1]. The average size of the obtained samples was estimated by the Zetasizer Nano ZS dynamic light scattering method (Malvern, UK). The absorption spectra of the samples were recorded on a UV Probe 3600 spectrophotometer (Shimadzu, Japan). Photoluminescence spectra were recorded on a Cary Eclipse spectrofluorimeter (Varian, Australia), magnetic circular dichroism spectra were recorded on a J-1500 JASCO.

As a result of the study, nanosized particles and core-shell composites based on magnetite and a semiconductor shell were obtained and characterized. Absorption, luminescence, dynamic light scattering, and magnetic circular dichroism spectra were measured. In continuation of the work, it is planned to reproduce the synthesis, as well as to consider various approaches to the creation of magnetic-luminescent nanocomposites.

[1] L. Liu, J. of nanos. and nanotech. 14, 5047 (2014).

Control of optical properties by change in surface chemistry of carbon dots based on citric acid and ethylenediamine

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Carbon dots (CDs) represent a new family of carbon luminescent nanomaterials consisting of carbon domains in sp²- and/or sp³- hybridization (sp²- and/or sp³- domains) containing many functional groups with oxygen, nitrogen, etc. at the edges of the domains and/or on the surface of the insulation [1].

In this work, special attention is paid to the study of the CDs morphology, optical and electrical properties depending on the type of added moieties, among which were benzoic acid (BA), citric acid (CA), UREA and o-phenylenediamine (o-pd). A study of the CDs surface chemistry has also been conducted providing additional information about the electronic subsystem of such nanoparticles.

CDs were synthesized using the solvothermal method, where CA and ethylenediamine (EDA) were selected as precursors in a molar ratio of 1:0.33. Water was used as a solvent. The resulting solution of precursors was heated in an autoclave at a temperature of 190 °C for 8 h. The final colloidal solution was purified from large particles and agglomerates using a syringe filter and further purified from small organic molecules using dialysis with a cut-off by weight of 6-8 kDa.

To estimate the influence of precursors (BA, CA, UREA and o-pd) on optical and electrical properties of CDs four samples were prepared: to 1 mL of CDs (1 mg/mL) a 2 g of each precursor, the mixtures were dissolved in 9 mL of water. The solutions were transferred into autoclaves, heated at 180 °C for 6h and cooled down to room temperature. Then colloidal solutions were purified from residual precursors via dialysis with a cut-off by weight of 6-8 kDa.

It was shown that in CDs samples with various additional substances, two absorption centers are observed, among which there is a shift to the longer-wavelength region relative to the first absorption center only in samples with CA and UREA. This may be because CA and UREA under hydrothermal conditions form molecular phosphors, which usually dominate the optical properties of CDs [2]. According to photoluminescence (PL) spectra a huge decrease in the PL intensity in samples with additional substances can be seen.

Morphology studies showed that functional groups on the surface of CDs mainly consist of groups such as O – H, C – H, C – O, C = O, and C = C. As a result, the appearance of new molecular groups on the surface makes it possible to control the electrical and optical properties of such nanostructures by change in their morphology.

This study was funded by Priority 2030 Federal Academic Leadership Program. XPS studies were conducted with financial support from St. Petersburg State University (project No 93021679).

[1] V. Nguyen, Carbon N. Y. Elsevier Ltd. 108, 268(2016).

[2] L. Dordevic, Nat. Nan. 17, 112(2022).

Semiconductor Materials Based on TiO_2 and $\text{g-C}_3\text{N}_4$ for Photocatalytic CO_2 Conversion

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Today, humankind faces the problem of utilization of greenhouse gases, especially CO_2 . CO_2 could be converted to more reactive compounds, such as CO and CH_4 by means of photocatalysis using renewable sources: light, CO_2 , and water. TiO_2 is well-known photocatalyst with high stability and low-cost, but with wide bandgap. $\text{g-C}_3\text{N}_4$ is a new perspective material obtaining a quite narrow bandgap. A deposition of transition metals (Pt, Cu, Ag) or its compounds (CuO , CuS , NiO) allow one to improve the photocatalytic activity.

This work is aimed at the synthesis and characterization of TiO_2 - and $\text{g-C}_3\text{N}_4$ -based photocatalysts modified with Pt and CuO_x . The reduction of CO_2 was studied under irradiation of light-emitting diodes with different wavelengths in the range from 380 to 425 nm, and the catalysts were characterized by transmission electron microscopy, X-ray photoelectron spectroscopy, and UV-Vis spectroscopy.

Commercial titanium dioxide Evonik P25 was used for photocatalyst preparation. For thermal activation, TiO_2 was pre-calcined at 700 °C for 3 h. $\text{g-C}_3\text{N}_4$ was synthesized from melamine by heating at 600 °C for 2 h. Pt and CuO_x were deposited on the surface of prepared photocatalysts by impregnation with H_2PtCl_6 or $\text{Cu}(\text{NO}_3)_2$ followed by reduction with a 2.5-fold excess of NaBH_4 . The reduction of CO_2 was carried out in a batch reactor (70 mL) with a quartz window (16 cm^2) under light irradiation. Gas probe was analyzed with a gas chromatograph “GH-1000” (Chromos, Russia).

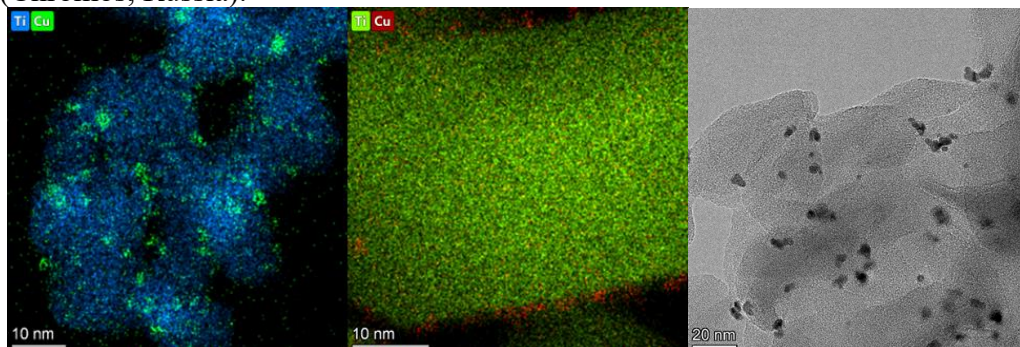


Fig. 1. Elemental X-ray mapping of 5% $\text{CuO}_x/\text{TiO}_2$ (left), 5% $\text{CuO}_x/\text{TiO}_2$ pre-calcined at 700 °C (center), and HR TEM image of 1%Pt/ $\text{g-C}_3\text{N}_4$ (right).

Platinum was in the metallic state on the surface of both TiO_2 and $\text{g-C}_3\text{N}_4$ samples. Copper was present in various states (Cu^0 , Cu^{+1} , Cu^{+2}). Thermal activation of TiO_2 promotes a uniform distribution of cocatalyst, which is beneficial for the CH_4 production under irradiation of visible light. The highest CO_2 reduction rate was 37 $\mu\text{mol h}^{-1} \text{g}^{-1}$, achieved over Cu/TiO_2 under light irradiation with a maximum intensity of 400 nm.

This study was supported by Russian Science Foundation (Grant #21-73-10235).

Influence of IR-heating rate on structure and magnetic properties of FeCoNi/C nanocomposites

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Nanostructured ferromagnetic materials are promising and widely used. The creation of carbon composite materials with modifiable structure and properties on the basis of diverse organic substrates, as well as the development of the method of obtaining the FeCoNi/C nanocomposites with controllable structure and properties (catalytic, magnetic, and radar-absorbent), based on the simultaneously proceeding synthesis of metal nanoparticles and carbonization of polymers with the formation of carbon matrix stabilizing the nanoparticles, are also topical directions. [1] One of the significant parameters while heat treatment is heating rate. In this work, the influence of the heating rate on structure and properties of the FeCoNi/C nanocomposites has been studied.

Metal-carbon nanocomposites FeCoNi/C (Fe:Co:Ni = 50:40:10) have been synthesized from the metal-organic precursor, which was obtained by joint dissolution of polyacrylonitrile (PAN) and the nitrates in dimethylformamide (DMF) with the subsequent desiccation at $T \approx 70$ °C. The solid sediment has been IR-pyrolyzed in the N₂-atmosphere in MILA 5000 facility at $T = 700$ °C. The four heating rates — 10, 30, 70, and 100 °C/min — have been considered.

XRF-analysis has shown that the composition of metal phases and the average size of nanoparticles with the FCC-type of crystal lattice ($d \approx 11$ -13 nm) in the metal-carbon nanocomposites are almost unchanging in the range of heating rates of 10-100 °C/min. Similarly, the average size of nanoparticles with BCC-type lattice ($d \approx 9$ -11 nm), having the common tendency for reducing. The studies have also shown that no critical influence of the heating rate on the structure is seen. The magnetic properties of the powders have been measured on the Lakeshore 7407 vibrating-sample magnetometer at ambient temperature.

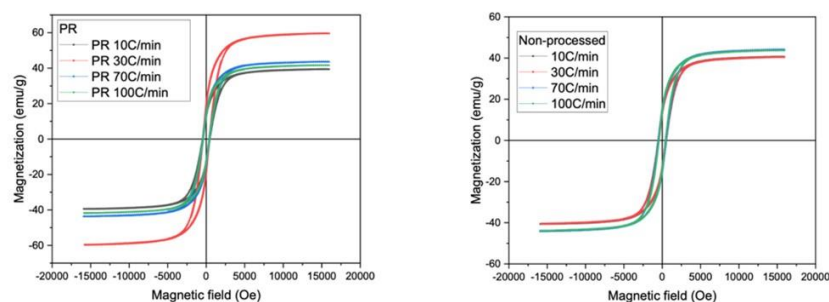


Fig. 1. Hysteresis loops of processed (left) and non-processed (right) samples

The increase of saturation magnetization while heating rate increases from 10 to 30 °C/min for processed samples and its slight decrease at 70-100 °C/min is shown in the measurements given. Similarly, remanent magnetization decreases. For the non-processed samples changes are opposite, but less significant. Coercive force of all the types of materials decreases (fig. 1). The changes are defined by the composition of metal phases and size of nanoparticles of the FeCoNi alloys.

[1] L. V. Kozhitov, I. V. Zaporotskova, D. G. Muratov, N. P. Boroznina, A. V. Popkova, S. V. Boroznin, E. V. Yakushko / Synthesis, properties and modelling of metal-carbon nanocomposites // Monography. Volgograd: Volgograd State University Publishing. — 2019.

Amplification of the bioluminescence signal by gold nanoparticles

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In this work, we studied the effect of silver and gold nanoparticles on the bioluminescent system of fireflies, as well as on the extraction of ATP from bacterial cells. It has been shown that the use of gold nanoparticles leads to an increase in the bioluminescent signal, which can be explained by the theory of metal-enhanced bioluminescence [1].

In this work, extraction solutions containing gold and silver nanoparticles stabilized with BAC (benzalkonium chloride) and Triton (Triton X-100) detergents were used. It has been suggested that an extraction buffer based on detergent-stabilized metal nanoparticles is more efficient than a buffer based on the same detergents. The use of nanoparticles stabilized and coated with detergents should increase the contact area of detergents with the cell membrane and increase the efficiency of bacterial cell lysis.

Silver nanoparticles were obtained by adding sodium borohydride to an aqueous solution containing silver nitrate and detergents. Gold nanoparticles were obtained by the same methods, but using tetrachlorouric acid. After that, the metal nanoparticles were washed and used for ATP extraction. Measurements were taken immediately after mixing the bacterial suspension and extraction buffers and 10 minutes after the start of extraction.

When studying the effect of nanoparticles on a bioluminescent system, we found that washed gold nanoparticles stabilized with BAC and unwashed gold nanoparticles stabilized with Triton enhanced the bioluminescent signal. This can be explained by the theories of the FRET effect and the effect of fluorescence enhancement by metals. Thus, when using gold nanoparticles, the sensitivity of the biosensor based on the glow reaction of fireflies can be increased.

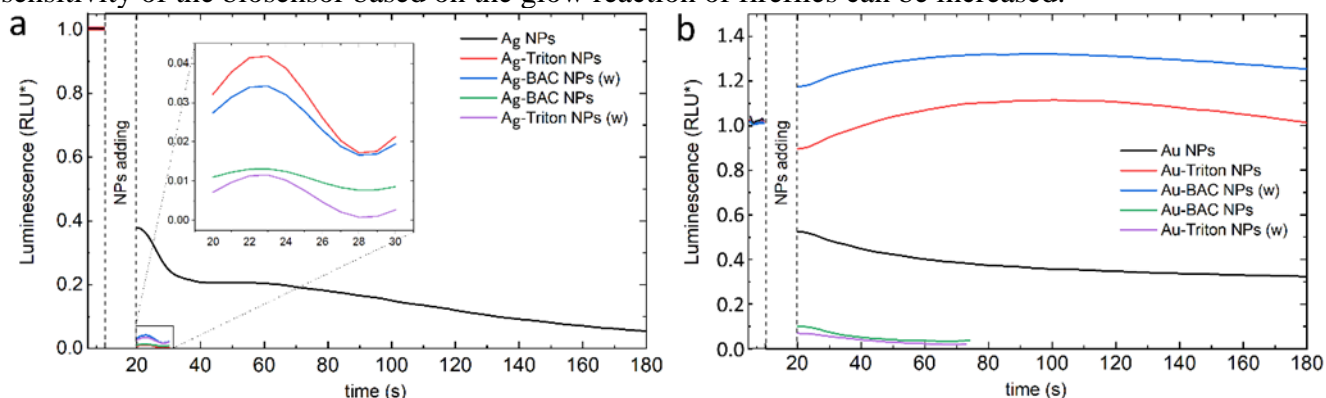


Figure 1. Effect of silver and gold nanoparticles on a bioluminescent system.

[1] E. Eltzov, D. Prilutsky, A. Kushmaro, R.S. Marks, C.D. Geddes, Metal-enhanced bioluminescence: An approach for monitoring biological luminescent processes, Appl. Phys. Lett. 94 (2009). <https://doi.org/10.1063/1.3086283>.

Complex Thermal Behavior of Exchange Bias in Ni-Mn/Fe-Ni Films

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Sixty-five years after its discovery, exchange bias remains one of the unsolved mysteries in magnetism, as no model can successfully account for all its peculiarities [1]. The effect, widely used in microelectronics, from sensors to magnetic memory devices, manifests as a shift of a hysteresis loop of a ferromagnetic part of a ferromagnet/antiferromagnet film by a value of the exchange bias field H_{EX} . The existing models of exchange bias include the spin glass model, which proposes the existence of a spin-glass-like phase on the interface to explain a pronounced increase in H_{EX} at low temperatures [2], and the polycrystalline model, which explains a gradual decrease of H_{EX} with temperature due the existence of a grain-size distribution in an antiferromagnet [3].

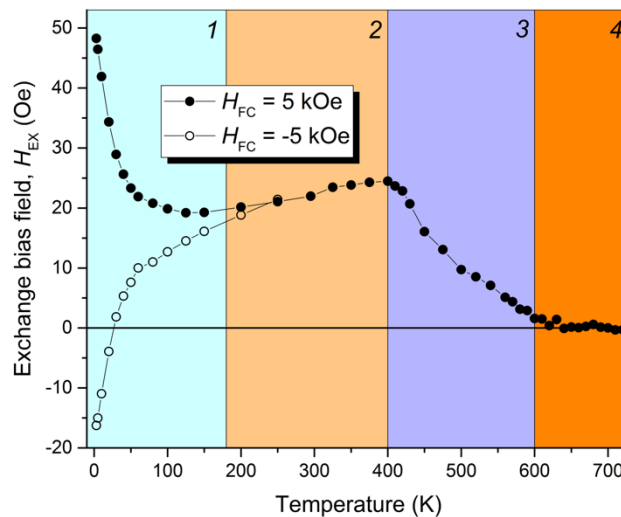


Fig. 1. Temperature dependence of the exchange bias field H_{EX} in a Ni-Mn (20 nm)/Fe-Ni (40 nm) film.

In this work we combine these models with conventional and *in situ* vibrating sample magnetometry and X-ray diffractometry to analyze what probably is the most complex thermal behavior of exchange bias in magnetron-sputtered Ni-Mn/Fe-Ni films. Fig. 1 represents a temperature dependence of H_{EX} in a Ni-Mn (20 nm)/Fe-Ni (40 nm) film. The films were annealed for 1 h at 300°C to promote the formation of the antiferromagnetic θ -NiMn. We establish that at each temperature range, denoted by a number, a different mechanism, or a combination of them is responsible for the picture observed. The low-temperature spike in H_{EX} (1) is due to the grain-size distribution in the spin-glass-like interfacial phase, the existence of which is confirmed by the temperature dependences upon field cooling in positive and negative magnetic fields (Fig. 1). The unusual rise in H_{EX} (2) is a consequence of an increase in the anisotropy constant in θ -NiMn, while the following decrease (3) is due to the polycrystalline nature of the film. Finally, the disappearance of H_{EX} (4) is accompanied by the decomposition of θ -NiMn.

[1] F. Radu, H. Zabel, Magnetic heterostructures, Springer, 97 (2008).

[2] V. Baltz, et al., Phys. Rev. B, **81**, 052404 (2010).

[3] K. O'Grady, L.E. Fernandez-Outon, G. Vallejo-Fernandez, JMMM, **322**, p.883 (2010).

COBALT FERRITE WITH GOLD NANOCOMPOSITE AS A POTENTIAL AGENT FOR PHOTOTHERMAL TREATMENT

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A nanocomposite consisting of arginine-coated gold nanoparticles surrounded by dihydrocaffeic acid-coated cobalt ferrite nanoparticles was first synthesized and investigated as a potential agent for photothermal treatment of Huh7 liver cancer cells.

A comprehensive study of nanocomposite particles' morphology and structural properties presents a narrow size distribution, morphological and structural stability over time [1]. Nanocomposite's stability in aqueous suspensions was increased by adding cobalt ferrite nanoparticles due to its superparamagnetic properties. The cytotoxic effect of nanocomposite was examined on the Huh7 cell line using the WST-1 assay before testing the photothermal treatment. The test results show decreasing of cells viability with rising of nanocomposite concentration and exposure time from 6 h to 48 h which indicates an increase in the cytotoxic effect.

The nanocomposite was diluted in DMEM cell medium and added to the cell suspension at three concentrations: 10, 50, and 100 µg/mL. After a 24-hour exposure to the nanocomposite, the cell suspension was kept under the action of a laser with a wavelength of 800 nm which corresponds to the tissue optical transparency region, and the elevated temperature of the cell suspension was measured using an experimental setup. The effect of photothermal treatment on the cell suspension, measured using the WST-1 test, shows a decrease in cell viability by more than 50% (Fig. 1).

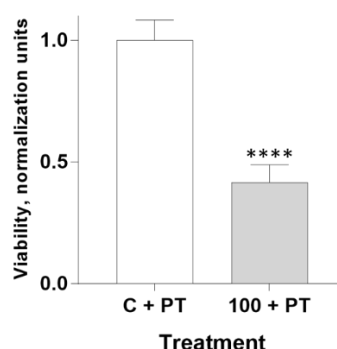


Fig. 1. Relative viability of Huh7 cell line after nanocomposite exposure for 24 h and photothermal treatment as a normalized units to the control data. The results shown are the mean \pm standard deviation. Columns marked with asterisks indicate results that were statistically different from controls: **** $P < 0.0001$. Statistical analysis was carried out using the One-way ANOVA

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[1] A.V. Motorzhina et al., Processes 9, 2264 (2021).

Synthesis, properties, application of magnetoactive metallopolymer nanocomposites containing Co, Ni and Fe

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The aim of this work is to obtain and investigate new functional magnetic metallopolymer nanomaterials of a new generation containing Co (II), Ni (II) and Fe and having increased level of consumer properties and qualities by thermolysis of precursors previously synthesized by us that is unsaturated dicarboxylates of these metals. A feature of the obtained nanocomposites is the solution of the actual problem of simultaneous synthesis and stabilization of NPs even at the stage of production by uniform distribution of NPs in the polymer matrix and the formation of a protective polymer shell of the core-shell structure. We assumed and proved the possibility of predicting and controlling the sizes of NPs and the output magnetic characteristics of the obtaining nanocomposites at the stage of obtaining to control the predominance of the ferromagnetic nature of the nanomaterial over the superparamagnetic one, depending on the initial conditions of thermolysis using Ni itaconate as an example.

In this work, 21 dicarboxylates and 21 nanocomposites were synthesized. Magnetoactive metallopolymeric Co, Ni and Fe nanocomposites obtained by controlled thermolysis at a temperature $335 \pm 1^\circ\text{C}$ under an argon atmosphere of a number of previously synthesized and characterized by us unsaturated dicarboxylates of these metals (allylmalonates (Almal), acetylenedicarboxylates, glutaconates, itaconates (It), maleates, cis,cis-muconates, citraconates), are powders consisting of two structure elements, namely, in organic polymer matrix containing fragments $-\text{CH}_2-$, $=\text{CH}-$ и $=\text{C}=$ the spherical NPs of $\text{Co}_3\text{O}_4/\text{CoO}/\alpha\text{-Co}$, $\text{NiO}/\beta\text{-Ni}$ or $\gamma\text{-Fe}_2\text{O}_3$ in the polymer shell of the core-shell structure are embedded. It was established that the thermolysis of ItNi leads to the formation of carbon nanotubes. The enthalpy (ΔH°_r) of formation reaction of Co, Ni and Fe carboxylates by the PM3 semi-empirical quantum-chemical method with using the HyperChem 8.0.8 (Hypercube Inc.) were calculated. The average NPs diameter (d_{adv}) of the obtained nanocomposites, namely 4-9 nm, was determined. A relationship between d_{adv} and ΔH°_r of Co, Ni and Fe carboxylates was established. The microstructure and magnetic characteristics of the obtained nanocomposites were determined. The highest coercive force is observed for nanocomposites based ItCo (1040 Oe), ItFe (119 Oe) and AlmalNi (131 Oe). The critical value of the NPs d_{adv} for Co associated with the transition from multi-domain to single-domain particles was found to be 3.8 nm.

The range of potential applications of the obtained nanocomposites is from gas and magnetic sensors, catalysts, high-density magnetic storage media to new forms of drugs and medical diagnostics. Studies were carried out on the cultivation of cell cultures of soil-forming micromycetes (*Trichoderma asperellum*, *Fusarium oxysporum*, *Aspergillus niger* and *Phytophthora infectans*), as well as human tumor cells HepG2 and HeLa on media containing synthesized Co, Ni and Fe nanocomposites. The possible joint use of Ammifurin and these nanocomposites as potential antitumor drugs is of interest from the results of colorimetric tests. The test intramuscular injections of magnetic Fe and Ni nanocomposites in mice line in amounts of $2 \cdot 10^{-6}$ g/g of weight didn't reveal any toxic effects. This work was supported by the Russian Foundation for Basic Research (project 13-03-00342 and 19-03-00237).

Hybrid electrospun poly(l-lactic acid)/reduced graphene oxide scaffolds with improved piezoelectric response

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Abstract

This work is focused on revealing the effect of reduced graphene oxide (rGO) addition on the morphology, structure, thermal behavior and piezoelectric performance of electrospun poly-L-lactide (PLLA) scaffolds.

Methods

To study the samples, scanning electron microscopy (SEM), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), Differential Scanning Calorimetry (DSC), piezoresponse force microscopy (PFM) were used.

Results and discussion

The SEM results reveal randomly oriented and defect-free hybrid PLLA-rGO fibers. The XPS results confirm the presence of rGO in the surface layers of the PLLA microfibers. Results of Raman spectroscopy allow concluding that molecular interactions occur. Despite the revealed nanocrystalline structure for all composite fibers, PLLA-1.0 the largest degree of crystallinity (22 %) of microfibers, thus, rGO filler promotes nucleation of the crystalline phase of PLLA. The effective out-of-plane and in-plane piezoresponses of the PLLA fibers are enhanced 2.3 and 15.4 times, respectively, by the addition of 0.2 wt.% rGO, in comparison with pure PLLA ones.

This research project was supported by the Russian Science Foundation under grant No 22-13-20043 <https://www.rscf.ru/project/22-13-20043/> and funded by the Administration of the Tomsk Region. The authors acknowledge the help of A.M.S. Jekhan for results discussion.

Ultrafast modulation of optical transmission during excitation of plasmon lattice modes in a metasurface based on Bi:YIG-Au

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Currently, the modulation of material properties using high-power lasers is used to study ultrafast processes. To study such processes, the “pump-probe” technique is used. An ultrashort laser pulse of high peak power causes heating of the electron gas in metals and a change in the dielectric permittivity [1]. As a result, the transmittance changes on sub-picosecond timescale. To investigate the process, the differential transmittance is measured. This value is defined as

$$\frac{\Delta T}{T} = \frac{T_{pump} - T_0}{T_0}, \quad (1)$$

where T_{pump} is transmittance t in the presence of pumping pulse, T_0 is transmittance in the absence. The exposure of laser radiation on an array of spatially ordered nanoparticles causes the excitation of surface plasmon resonances (SLR). Excitation of SLR and other resonant modes leads to an amplification of ultrafast modulation of optical properties [2].

In our work, differential transmittance spectra of magnetoplasmonic metasurface were measured by the “pump-probe” technique at various delay times. The sample was a two-dimensional periodic square lattice of gold nanospheres covered by a layer of bismuth-substituted iron-yttrium garnet (Bi:YIG). Magneto-optical properties of the sample had been investigated in article [3]. Dependence of the differential transmittance on the fluence of incident radiation in the range from 0.1 to 0.8 mJ/cm² was also investigated.

There are several resonant features on the spectrum of the differential transmittance: at 530 nm there is a quasi-waveguide mode in the garnet layer, at 615 nm and 730 nm there are quadrupole and dipole lattice plasmon resonances in the gold nanospheres. With a normally incident probe beam, the pump pulse was in resonance. At polar and azimuthal angles of 18 degrees, the pump pulse showed no resonant effects. The form of the spectrum at these angles is similar, however at the same power, the effect for indirect incidence is approximately 3 times weaker. Differential transmittance dependence on laser fluence shows non-linear behavior in the several spectral regions. In the same regions extraordinary transmittance dynamics is observed.

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- [1] Sun C.K. et al. Femtosecond investigation of electron thermalization in gold // Phys. Rev. B – 1993. – Vol. 48, p. 12365.
- [2] Gregory V Hartland, Optical studies of dynamics in noble metal nanostructures // Chem. Rev. – 2011. – Vol. 111, 6.– p. 3858–3887.
- [3] Musorin A. I. et al. Tunable multimodal magnetoplasmonic metasurfaces // Appl. Phys. Lett. – 2019. – T. 115. – №. 15. – C. 151102.

Polyanion compounds-based carbon containing composites as frameworks for alkali-metal ion de/intercalation

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Nowadays great number of everyday devices and vehicles are powered by rechargeable batteries. Nevertheless, the concept of metal-ion battery has been known since 1990-s, there is still a room for further improvement of existing materials and synthesis of new ones. Among all of relatively new classes of electrode materials, polyanions demonstrate vast perspectives in number areas of applications, for example, in stationary energy storage [1].

At the same time, due to their nature the most polyanions demonstrate weak electronic conductivity – pure, phases usually demonstrate insufficient cycling performance. Thus, preparation of specific composites, consisting of electrochemically active compound, binder and conductive additive is necessary in aim to achieve desirable performance. Many various sources of carbon and conductive additives were tested, part of them are acceptable only at the scale of laboratory due to the high price or issues related with further up-scaling. Typical sources of carbon additive are various forms of carbohydrates, such as, sugar or organic acids (citric, ascorbic etc.) and great variety of macromolecules [2]. Not only the source, but the way the sample is covered determines it's electrochemical performance.

The aim of this work is synthesis through combined method of fluoride-phosphates crystallizing in KTiOPO_4 crystal type. The typical samples, $\text{KVPO}_4\text{F/C}$ composite were synthesized in two steps. At the first one, solution of precursors (V, phosphate anions, organic additive) were lyophilized and the resulting powder was annealed in Ar flow at 750 °C. The resulting black powder was mixed with stoichiometric amount of KHF_2 and further treated at 600 °C for 2 hours. The residual amount of carbon content was calculated according to the TG-DSC data. Electrochemical properties of composites were investigated in K-half cell in a potential range 3.5-5.0 V vs. K^+/K in. The sample containing 9% of residual carbon (figure 1, right) demonstrate discharge capacity 100 $\text{mAh}\cdot\text{g}^{-1}$ with an average operating potential 4.3 V vs. K^+/K , which is in agreement with literature data. This result for such synthesis approach was demonstrated for the first time [3].

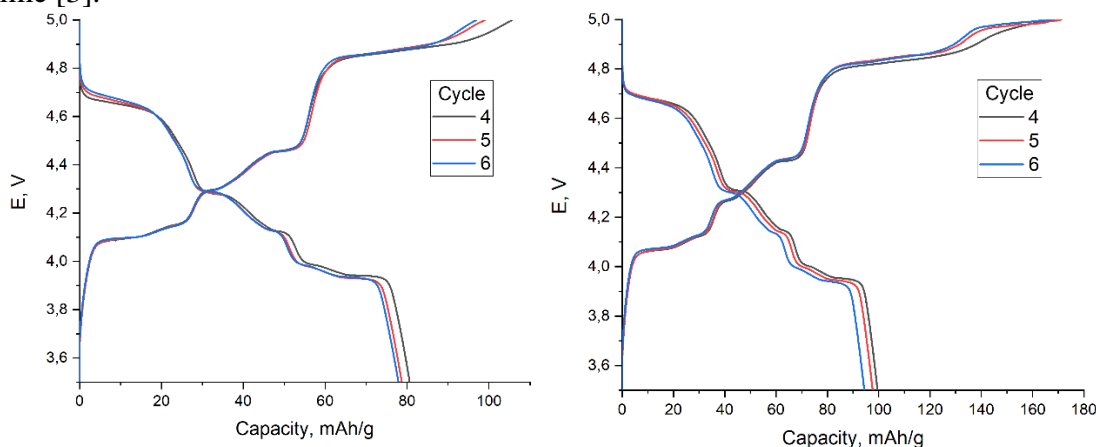


Figure 1. Galvanostatic charge-discharge curves of $\text{KVPO}_4\text{F/C}$ (7% and 9% of residual C respectively).

- [1] C. Masquelier, L. Croguennec, Chemical Reviews 113.8 (2013).
- [2] J. Ni, L. Zhang, S. Fu, S. V. Saviolov, S. M. Aldoshin, L. Lu, Carbon, 92 (2015).
- [3] H. Kim, Y. Tian, G. Ceder, Journal of the electrochemical society 167.11(2020).

Magnetoimpedance properties of amorphous materials of various shapes

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In recent years, more and more attention has been paid to the study of various amorphous materials [1]. This is due to the fact that these materials have unique sets and combinations of properties, due to which they are widely used in microelectronics, instrumentation and medicine [2]. Their pronounced magnetic softness and good mechanical properties make them promising for the design of soft magnetic composites composite structures, as well as for the manufacture of various sensors and actuators [3,4]. The effect of giant magnetoimpedance (variation of impedance under magnetic field application) reaches as much as 600% [5] and allows the construction of highly sensitive magnetic field sensors working at room temperature [6].

GMI effect was reported to be very sensitive to the micromagnetic structure of amorphous alloy [7]. Thus, combined with traditional magnetometry GMI method is an effective tool for studying the magnetic and structural properties of various materials [8].

One of the important factors affecting the micromagnetic structure and, consequently, GMI characteristics is the shape of the element. Currently, the most investigated magnetoimpedance elements are amorphous ribbons and microwires. The change in shape of wires and ribbons can affect the structure and the effect of giant magnetoimpedance. With this in mind it is possible to increase the sensitivity and operating range of the sensors.

In this research, the magnetoimpedance characteristics of FeSiB glass-coated conical amorphous microwires of the diameters 20 μm , 33 μm 48 μm with conicity 1:100000, as well as micro-springs made of amorphous microwires with core diameter 525 μm , 542 μm , 568 μm , 712 μm , were investigated. The measurements of impedance were carried out using VNA FieldFox Agilent N9923A at room temperature in the frequency range up to 500 MHz under magnetic fields up to 400 Oe.

It is found that the GMI field dependences have a pronounced asymmetry (the magnitude of the impedance depends on the direction of the field) and the direction of twisting of the springs.

As for the wires the measurements have shown that the value of GMI in conical micro-wires increases with increasing wire diameter, and also that there is no influence of the direction of the taper of the wires on the parameters of the GMI dependencies

The possibilities of applying the obtained effect in the development of new types of sensors and actuators are discussed.

[1] H.R. Lashgari et al., "Composition dependence of the microstructure and soft magnetic properties of Fe-based amorphous/nanocrystalline alloys: A review study", *Journal of Non-Crystalline Solids*, 391 (2014), 61-82.

[2] D. Azuma, N. Ito, M. Ohta, "Recent progress in Fe-based amorphous and nanocrystalline soft magnetic materials", *JMMM*, 501 (2020), 166373.

[3] Yi Cao et al., "High-frequency magnetic characteristics and operating thermal stability of industrialized Fe₇₆Si₁₃B₈Nb₂Cu₁ nanocrystalline alloy ", *JMMM*, 526 (2021), 167691.

[4] M.H. Cohen, D. Turnbull, "Metastability of Amorphous Structures", *Nature*, 203 (1964), 964.

[5] P. Corte-Leon et al., "Magnetic Microwires with Unique Combination of Magnetic Properties Suitable for Various Magnetic Sensor Applications", *Sensors*, 20 (2020), 7203.

[6] K. Mohri et al., "Amorphous wire and CMOS IC-based sensitive micro-magnetic sensors (MI sensor and SI sensor) for intelligent measurements and controls", *JMMM*, 249 (2002) 351–356

[7] A. Zhukov et al., "Giant magnetoimpedance in rapidly quenched materials", *Jallcom*, 814 (2020)

[8] E. Lopatina et al., "Surface crystallization and magnetic properties of Fe_{84.3}Cu_{0.7}Si₄B₈P₃ soft magnetic ribbons", *Acta Materialia*, 96 (2015), 10–17.

Influence of microcrystalline cellulose on the structural and physico-chemical properties of ionogels based on Na-bentonite and 1-butyl-3-methylimidazolium acetate ionogels

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In recent years, there has been a rapid development of a new field of research dedicated to the creation of biopolymer nanocomposites from renewable sources, due to growing environmental concerns and a decrease in fossil resources.

Ionogels based on ionic liquid (IL) and clay minerals are promising candidates for creating the next generation of electrolytes and can be used to obtain new types of electrochemical devices due to their high ionic conductivity, lack of fluidity, fire resistance and environmental friendliness. But, when obtaining these materials, one may encounter a rather significant drawback - they are fragile.

To solve this problem, we proposed, at the stage of mixing clay with IL, to dissolve microcrystalline cellulose (MCP) in the latter. This will help not only to improve the stabilization of the gel-like state of IL during the formation of frameworks from clay nanoparticles in a liquid matrix, but also to enhance adsorption interactions at the interface. Due to limiting effects, these ionogels change their fluidity, viscosity, thermal and structural properties [1].

Scanning electron microscopy data showed that ionogels based on the ternary IL/MCR/Na-bentonite system have a more ordered structure compared to the IL/Na-bentonite ionogel, and the clay particles in it are evenly distributed in the liquid matrix.

According to the diffraction patterns of the studied samples, all ionogels were characterized by the presence of reflections of different intensity, at angles $2\Theta=8.48^\circ\text{C}$ for an ionogel based on IL/Na-bentonite, and 8.86°C for three-component ionogels, respectively. They reflect the formation of structurally ordered IL crystallites between clay particles. It should be noted that with an increase in the concentration of cellulose in the ionogel, the intensity of these reflections also increases.

The data of thermogravimetric studies proved that MCR enhances the adsorption interaction between IL and Na-bentonite particles, which leads to an increase in the temperature range of decomposition of IL adsorbed on the clay surface by almost 20°C .

Thus, the introduction of MCR into the ionogel allows not only to improve the plasticity and viscosity of the material, but also has a positive effect on other equally important properties of these nanocomposites, which will also increase their scope in various industries.

[1] A.V. Agafonov, V.D. Shibaeva, A.S. Kraev, S.S. Guseinov, L.M. Ramenskaya, N.O. Kudryakova, E.P. Grishina. *Journal of Molecular Liquids*, 2020, **315**, 113703—113712.

Synthesis and properties of heteroacenes for organic electronics

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Organic electronics has been actively developed in recent years due to their advantages such as ease of processing, low manufacturing cost, and mechanical flexibility. Among a large variety of organic semiconductors, heteroacenes (Fig.1) have been widely investigated as promising organic semiconductors in high-performance OFETs. Fused-thiophene structure lead to unique properties, such as extensive conjugation, strong intermolecular S–S interactions, and rigid coplanar conjugated core, which contributes to attractive charge-transfer properties.

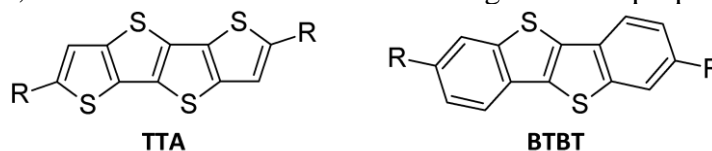


Fig. 1. Structural formulas of tetrathienoacene (TTA) and benzothienobenzothiophene (BTBT) derivatives.

This work describes the synthesis, properties and application of new aliphatic and aromatic derivatives of heteroacenes in various optoelectronic devices - . The characteristics of organic field-effect transistors based on them, obtained by both solution and vacuum methods, have been investigated. Fast and simple technique based on Doctor Blade and Langmuir-Schaefer methods for functionalization of the semiconducting surface of C8-BTBT-C8 allowing to fabricate large scale biorecognition layer based on the novel functional derivative of BTBT containing biotin fragment as a foundation for further biomodification . As a proof-of-concept, we demonstrate the specific response of the BTBT-based biorecognition layer in EGOFETs to a virus of influenza A (H7N1 strain). The influence of dynamic disorder on charge transfer inside annelated organic semiconductors is also discussed .

This work was supported by RSF (project № 19-73-30028).

- [1] Borshchev O.V, Skorotetskiy M.S., Trukhanov V.A. et. al. Dyes Pigm. 2021, 185, 108911
- [2] Skorotetskiy M.S., Borshchev O.V, Polinskaya M.S. et. al. J. Mater. Chem. C 2021, 9, 10216
- [3] Nikita V. Prudnikov, Yulia N. Malakhova, Andrey V. Emelyanov et. al. Phys. Status Solidi RRL, 2022, 2100471
- [4] Poimanova, E.Yu.; Shaposhnik, P.A.; Anisimov, D.S. et.al. ACS Appl. Mater. Interfaces, 2022, 14, 14, 16462
- [5] Sosorev A.Y., Parashchuk O.D., Tukachev N.V. et. al. Phys. Chem. Chem. Phys. 2021 accepted

Mangiferin-Loaded Nanofibers Based on Hyaluronic Acid

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Hyaluronic acid (HA) is a natural heteropolysaccharide consisting of a multiple disaccharide structure of N-acetyl-D-glucosamine and D-glucuronic acid [1]. Due to its specific physico-chemical, rheological, chemical properties and relevant biological requirements, HA is used in various medical fields, including regenerative medicine and tissue engineering, as well as in targeted drug delivery [2].

Mangiferin is a biologically active xanthone derivative present as a glycoside in various plant species, including *Mangifera indica* [3]. Despite its wide pharmacological potential, mangiferin has poor solubility, transmembrane permeability, and bioavailability, which limits its practical application in medicine [4]. One method to improve the efficacy of mangiferin is to integrate (encapsulate) the biologically active compound into a polymer matrix resulting in the obtaining of drug delivery system. Electrospinning is an effective and unexpensive method for obtaining polymer drug delivery systems such as nanofibers and nanoparticles.

Rheological properties and electrical conductivity are important characteristics of polymer solutions, determining the possibility of using such solutions for the formation of polymer nanofibers by electrospinning technique. To investigate these properties, 1.9 mass.% aqueous-organic solutions of HA with the addition of mangiferin in mass ratios of 19:1, 13:1, 9.5:1 and 8:1 respectively were prepared. The conductivity was measured on a Mettler Toledo SevenCompac pH/Cond S213 instrument at room temperature 24 ± 2 °C. The study showed that the addition of mangiferin increased the electrical conductivity of HA solutions. The dynamic viscosity was measured on an Anton Paar Physica MCR 502 rotary rheometer with a cylindrical measuring system at shear rates from 0.1 s^{-1} to 100 s^{-1} in the temperature range from 25°C to 40°C. Plots of the dependence of the dynamic viscosity of the solutions studied on the shear rate at different temperatures were plotted. These graphs show that increasing the temperature and shear rate decreases the dynamic viscosity of the solutions, while increasing the mangiferin content in the solutions increases their dynamic viscosity.

Nanofibers were obtained for the first time from the investigated aqueous-organic solutions by electrospinning using NANON-01A system. It was possible to obtain smooth and low-defect fibers from polymer solutions with a mass ratio of HA:mangiferin 8:1, 9.5:1 and 13:1. The average diameter of these nanofibers was equal to 0.8 μm .

The developed nanofibers have topical and high-effective potential application as burn and wound regenerative coatings and mangiferin transdermal delivery systems, which will promote the transition to personalized medicine and modern healthcare technology.

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[1] J. Necas, Veterinarni Medicina. 53(8), 397, (2008).

[2] A. Fallacara, Polymers. 7(7), 701, (2018).

[3] A. Vyas, Mini Rev. Med. Chem. 12(5), 412, (2012).

[4] S. Du, Molecular Medicine Reports. 18(6), 4775 (2018).

Scanning probe microscopy and X-ray computed tomography: non-trivial approaches to study composite materials

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Polymer-based composite materials with embedded ferromagnetic and/or ferroelectric filler particles are the intriguing class of materials due to the high applicability potential in a number of areas: magnetic field sensors, energy harvesting, biomedical devices, etc. [1]. In the later case the combination of piezoelectric, magnetic and mechanical properties of such composites make them promising as bioactive scaffold surfaces for neural stem cell cultures [2,3]. However, the desired combination of properties strongly depends not only on the type of the matrix and the fillers, but also on the configuration of the arrangement of filler particles inside the polymer and the effect this arrangement has on the inner structure of the polymer chains [4]. This issue has to be carefully studied and not every experimental technique provides the possibility to do that.

Scanning probe microscopy (including atomic-force, magnetic-force, piezoelectric-force, etc. microscopy) is a multifunctional tool to study mechanical, magnetic, piezoelectric and stricitive response of composite materials. The main advantage of SPM is the possibility to examine the desired properties in conjunction which is helpful for such classes of materials as multiferroics where magnetic, electric and elastic properties are strongly interconnected. Another advantage is the ability to map the studied properties across the sample surface.

X-ray computed tomography (XCT) is another useful technique to study both static and dynamic properties of polymer-based composite materials. High resolution XCT can be used to obtain the three dimensional mapping of the X-ray optical density in the volume of the samples, thus visualizing the distribution of the filler particles in the matrix. The spacial resolution in this case can reach 1 μm , enabling to effectively establish the way filler particles are located inside the polymer.

In this work, taking PVDF-TrFE polymer-based piezoelectric elastic composite with $\text{Zn}_{0.25}\text{Co}_{0.75}\text{Fe}_2\text{O}_4$ and/or BaTiO_3 fillers as an example, we investigated how SPM and XCT approaches can be used for the study of composite materials. We studied the mechanical and magnetic properties on the composites using NTEGRA scanning probe microscope (HT-MDT, Russia) and the distribution of filler particles using XCT YXLON (Cheetah, Germany). We associated the structuring, observed by XCT, with the inner structure of the matrix and, thus, the observed properties. The obtained results let us conclude on the mechanisms of the interaction between the particles and the matrix and gave us the important insights about the formation of the properties in the studied class of composites.

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[1] Ze Q., et. al., Adv. Mater. 32, 1–8 (2020).

[2] Murzin D., et. al., Sensors 20, 1569 (2020).

[3] Roy K., et. al., ACS Appl. Nano Mater. 2, 2013–2025 (2019).

[4] Omelyanchik A., et. al., Nanomaterials 11(5), 1154 (2021).

Perovskite matrix influence on optical properties of Yb³⁺ doped CsPbCl_xBr_{3-x} perovskite nanocrystals

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A relevant task of modern science is the creation of new types of perovskite nanocrystals (NCs) and the subsequent study of their optical properties. A prospective direction in this field is the doping of NCs with different ions, including lanthanides, for instance ytterbium (Yb³⁺) ions. These nanostructured materials can be widely used in the creation of modern stable sources of near infrared (IR) radiation. Perovskite NCs have a number of valuable properties, such as intense photoluminescence (PL), high values of the absorption coefficient, stability and tolerance to defects [1]. Such materials can be used in the improvement of visualization methods, the creation of new-generation biological markers and sensors [2].

In the present work, the optical properties of perovskite NCs of the chemical composition CsPbCl_xBr_{3-x} doped with Yb³⁺ ions are studied [3]. Optical spectroscopy methods, including time-resolved luminescent spectroscopy, are used for these purposes. The chemical composition of NCs is modified by an anion exchange reaction with dodecyltrimethylammonium bromide. As a result, the band gap of NCs changes in accordance with the exchange degree of Cl⁻ anions for Br⁻ anions. In this case, the PL band of the NCs matrix shifts to the long-wavelength region of the spectrum. This shift is observed in the wavelength ranges from ~407 nm for the initial sample with Cl⁻ anions up to ~500 nm for the sample with the highest exchange degree of Cl⁻ anions for Br⁻ anions. It also leads to a change in the PL intensity of the Yb³⁺ doping ions and the perovskite NCs matrix.

The spectral and kinetic parameters of PL have been studied for the obtained perovskite NCs. The effect of the anion exchange reaction in the perovskite matrix on the optical properties of CsPbCl_xBr_{3-x} doped with Yb³⁺ ions has been determined. The anion exchange of Cl⁻ anions for Br⁻ anions leads to a change of PL quantum yield in the visible and near-IR spectral ranges, as well as PL decay times. The maximum PL quantum yield reaches 72% for a band gap value of 2.54 eV. These results can be used to obtain new nanomaterials with effective PL in a wide spectral range. It can be applied in optoelectronics, solar energy, and biomedicine.

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[1] Mei X. et al. Approaching high-performance light-emitting devices upon perovskite quantum dots: Advances and prospects // *Nano Today*. 2022. Vol. 43. P. 101449.

[2] Dey A. et al. State of the Art and Prospects for Halide Perovskite Nanocrystals // *ACS Nano*. 2021. Vol. 15, № 7. P. 10775–10981.

[3] Zhang X. et al. Yb₃ and Yb₃/Er₃ doping for near-infrared emission and improved stability of CsPbCl₃ nanocrystals // *Journal of Materials Chemistry C*. 2018. Vol. 6, № 37. P. 10101–10105.

New features of the Rutherford Backscattering Spectroscopy Method in nanotechnologies with the use of powders

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Rutherford Backscattering Spectrometry (RBS) is an ion scattering technique used for compositional thin film that are less than 1 μm thick analysis. During an RBS analysis, high-energy He^{2+} ions with energies in the region from several hundred kiloelectron-volts to 2 - 3 MeV are directed onto the sample and the energy distribution and yield of the backscattered He^{2+} ions at a given angle is measured. Since the backscattering cross-section for each element is known it is possible to obtain a quantitative compositional depth profile from the RBS spectrum obtained.

The capabilities of this method can be significantly expanded. In particular, the method can be used in powder nanotechnology to study elemental composition in microscopically small objects.

The application of methods based on Rutherford Backscattering Spectrometry is extremely interesting for adsorption energy devices, in particular, these methods can be used with maximum efficiency for various chemoelectronic converters.

A unique opportunity is to study the elemental surface of adsorbates on the surface phase separation in functional nanostructured layers.

For this reason, the preparation of planar-distributed chemoelectronic converters and the study of the elemental composition of adsorbates using the Rutherford Backscattering Spectrometry technique was the purpose for the investigation.

The tasks of this study included: development and optimization of the technology for producing planar chemoelectronic converters a functional layer in the form of rounded drops containing monodisperse nanosized (7.5 μm) particles of a solid solution of the ZrO_2 system - 3 mol% Y_2O_3 (YSZ) in the PVA polymer matrix, study of the theoretical characteristics of the obtained chemoelectronic converters [1], study of the elemental composition of the obtained chemoelectronic converters using Rutherford Backscattering Spectrometry.

The atomic and chemical composition of these layers has been studied using nuclear and atomic methods.

The thickness of the oxide layers was found to be approximately the same for all implanted samples. These values were determined on the basis of Rutherford Backscattering Spectrometry and nuclear reactions (RBS/NR).

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[1] L. Chemical-Electric Energy Conversion Effect in Zirconia Nanopowder Systems A. S. Doroshkevich, A. I. Lyubchyk, A. V. Shilo, T. Yu. Zelenyak, V. A. Glazunovae, V. V. Burhovetskiy, A. V. Saprykina, Kh. T. Holmurodov, I. K. Nosolev, V. S. Doroshkevich, G. K. Volkova, T. E. Konstantinova, V. I. Bodnarchuk, P. P. Gladyshev, V. A. Turchenko, S. A. Sinyakina. (2017). Journal of Surface Investigation: X-ray, Synchrotron and Neutron Techniques Vol. 11, No. 3. - Pp. 523–529. DOI: 10.1134/S1027451017030053.

Thermoelectric properties of the metal-ceramic composites based on Bi_2Te_3 - Bi_2Se_3 matrix and Co (cobalt) inclusions

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Currently, cermet composites (or cermets) consisting of ceramic matrix (Al_2O_3 , ZrO_2 , SiC , etc.) and metal filler (Cr, Ti, Al, Mo, etc.) are important type of composites, attractive for practice. One of promising approaches of modern thermoelectric materials science is based on developing thermoelectric magnetic cermets consisting of common thermoelectric taken as a ceramic matrix, and a metal filler possessing ferromagnetic properties (transition d-metals). The purpose of this research is to prepare novel thermoelectric magnetic cermet consisting of grained $\text{Bi}_2\text{Te}_{2.1}\text{Se}_{0.9}$ matrix and metal ferromagnetic Co filler, and to find and analyze the patterns of spark plasma sintering (SPS) temperature effect on features in the microstructure and thermoelectric properties of this cermet.

Novel cermet $\text{Bi}_2\text{Te}_{2.1}\text{Se}_{0.9}+0.33$ wt% Co composite has been prepared via spark plasma sintering (SPS) the starting $\text{Bi}_2\text{Te}_{2.1}\text{Se}_{0.9}$ and Co powders at different SPS-temperatures ($T = 598, 623, 648$ and 673 K). During the sintering, initial Co inclusions transform into final filler Co@CoTe_2 ("core"- "shell") inclusions, randomly distributed inside textured grained $\text{Bi}_2\text{Te}_{2.1}\text{Se}_{0.9}$ matrix. Forming these inclusions is originated from high- temperature chemical interaction between $\text{Bi}_2\text{Te}_{2.1}\text{Se}_{0.9}$ and Co. Main features in microstructure and thermoelectric properties of the cermet composite found with increasing TS are: (1) a texturing degree of grained $\text{Bi}_2\text{Te}_{2.1}\text{Se}_{0.9}$ matrix gradually decreases that is attributed to reducing in ability of initial nanometer Co particles to act as lubricant; (2) a fraction of the Co core decreases, and a fraction of the CoTe_2 shell increases that is related to acceleration of $\text{Co} \rightarrow \text{CoTe}_2$ reaction at higher temperatures; (3) the specific electrical resistivity and the Seebeck coefficient reduce, whereas the total thermal conductivity increases that can be originated from growth of electron concentration due to local Co doping. Highest value of the thermoelectric figure-of-merit equal to ~ 0.8 was observed for the composite, SPS-treated at 673 K.

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Formation of skyrmion states by ion implantation in CoPt and CoPd thin films

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It was previously found that ion implantation into thin CoPt films leads to asymmetric mixing of Co and Pt atoms, which causes a decrease in the perpendicular anisotropy of magnetization in structures leading to an increase in the Dzyaloshinskii–Moriya interaction, and contributing the activation of the formation of skyrmions [1]. In this work, we continued the studies by investigating the effect of ion implantation on the domain structure of ferromagnetic CoPt(2/5) and CoPd(2/5) thin films and on the appearance of skyrmion states in such structures.

The studied samples are Co_{0.35}Pt_{0.65} and Co_{0.35}Pd_{0.65} films. The Pt(Pd) (0.5 nm) and Co (0.2 nm) layers were deposited on i-GaAs substrates by electron-beam evaporation at 200°C (10 periods in total). The total thickness of metal films was ~7 nm. After the deposition process the structures were irradiated at the ILU-3 accelerator with He⁺ ions with an energy of 20 keV, while the fluence value (F) varied from 1×10^{14} to 3×10^{15} cm⁻². The magnetic field dependences of the Faraday angle (Q_F (H)) (at a wavelength of 980 nm) and the Hall effect (normal and planar) were studied at room temperature. The magnetic structure of the initial and irradiated samples was studied by magnetic force microscopy (MFM).

For the initial CoPt (2/5) film, the MFM image shows 1D skyrmions (360° domain walls ~100 nm wide). After the films are irradiated, a transition to round skyrmions is observed (at $F = 3 \times 10^{14}$ cm⁻²) as well as an increase in their number with increasing F. For a sample with a fluence of 7×10^{14} cm⁻², a very dense lattice of individual round skyrmions is revealed. At $F \geq 1 \times 10^{15}$ cm⁻², the lateral component of the magnetization vector begins to dominate. This fact is confirmed by measurements of the Hall and Faraday effects: the obtained dependences $Q_F(H)$ and $R_H(H)$ contain a hysteresis loop with a coercive field of ~ 600 Oe, while the Q_F value in the zero field coincides with the value in the saturation field, up to a fluence value of 5×10^{14} cm⁻². At higher values of fluence, a narrowing of the hysteresis loop and a decrease in the value of Q_F in zero magnetic field are observed, while at the maximum F, the Q_F (H) dependence becomes linear. According to measurements of the planar Hall effect, there is a monotonic decrease in the saturation field from 8000 Oe for the initial sample to 1500 Oe for the structure with $F = 3 \times 10^{15}$ cm⁻². The CoPd (2/5) films show a similar trend: one-dimensional skyrmions observed in the original sample become shorter with increasing fluence, and at $F = 1 \times 10^{15}$ cm⁻² they turn into “chains of round skyrmions”. Apparently, ion implantation changes the structure of domain walls. Thus the manipulation of skyrmion structure by varying the ion fluence in CoPt and CoPd films was demonstrated.

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[1] I. Kalentyeva, *et.al.*, Phys. Sol. St., **63**, 386-394 (2021).

Advanced Methods of Smart Materials Study Based on Optical and Atomic Force Microscopy Combination.

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Many groups of scientists put a lot of efforts to synthesize advanced materials which may be useful for people in a wide range of applications. Properties of these materials are determined at nanoscale level and should be studied by a propriate means. In other words, new materials require new microscopy methods to study surface and internal structure at nanoscale.

There are a lot of well-known microscopy methods like: optical, atomic force, electron microscopy and spectroscopy. Each of these methods have advantages and disadvantages which determine the field of application a particular tool.

Authors observe limitations of existing methods and offer the way to overcome it by the possibility of combination different methods in one tool.

Authors shows particular way of combination atomic-force microscopy and optical microscopy to reveal the magnetic domain structure with optical resolution under the diffraction limit Figure 1. It helps to avoid distortions in atomic force microscopy which may occur due to using the magnetic cantilever (cross remagnetization, external magnetic field influence etc). From the other hand this combine tool may improve optical resolution in magnetooptical mode by using near field scheme of measurements [1].

Authors observe the possibility of simultaneous measurements by the means of atomic force microscopy and Raman spectroscopy. This combination may provide scientists with more benefits than each of these methods separately. Composite materials based on polymers might be study by this combination tool. It may provide not only very precise information about topography of the polymers (AFM) but also its crystallinity, different components distribution and so on [2].

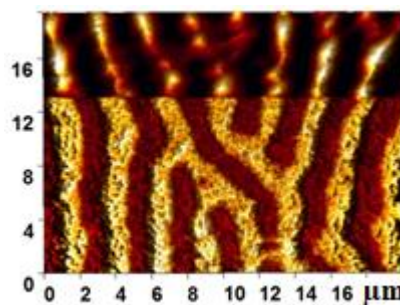


Figure 1. Magnetooptical image without (above) and with (below) combination with AFM.

[1] Yu. E. Vysokikh, T.V. Mikhailova, S. Yu. Krasnoborodko, A.S. Kolomiytsev, O.I. Ilin, A.N. Shaposhnikov, V.N. Berzhansky, M.F. Bulatov, D.V. Churikov, V.I. Shevyakov, JMMM 529 167837 (2021)

[2] <https://ntmdt-russia.com/home/products/ntegra-spectra/>

Microstructure Features of Metal-Matrix Composites Based on Thermoelectric Bismuth Telluride Matrix and Ferromagnetic Filler

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The formative predictables of the microstructure of metal-matrix composites, obtained using spark plasma sintering and consisting of polycrystalline thermoelectric bismuth telluride Bi₂Te₃ (composite matrix) and a ferromagnetic filler (Ni or Fe), were examined. It was determined that, in the course of spark plasma sintering, filler inclusions in the form of locally gradient inclusions of the nucleus–shell type (Ni@NiTe₂ and Fe@FeTe₂) are formed and randomly distributed in the Bi₂Te₃ textured matrix. The formation of NiTe₂ or FeTe₂ shells surrounding Ni or Fe nuclei, respectively, is associated with high-temperature diffusion redistribution of matrix atoms and initial filler inclusions during spark plasma sintering of the initial powders. This redistribution is accompanied by a chemical reaction of the formation of new NiTe₂ or FeTe₂ compounds. The basic parameters of the microstructure of composites (inclusion size and extent of texturing of the matrix) strongly depend on the filler content.

Spark plasma sintering of samples of the developed composites from the initial powders leads to the development of strong texturing in the samples, easily observed on SEM images of the grain structure obtained from the chipping of the surface oriented perpendicular and parallel to the direction of pressure application during spark plasma sintering.

Texturing samples is associated with the predominant ordering of grains in a plane oriented perpendicular to the direction of application of pressure during sintering (this direction is the axis of the texture). Texture formation is a typical phenomenon observed in polycrystalline compounds based on Bi₂Te₃, obtained using various technological methods based on uniaxial pressing of initial powders [13 - 17]. The granular structure is a lamellar structure, with the lamellar layers lying in a plane perpendicular to the direction of the pressure application. Lamellar layers consist of grains elongated in a plane parallel to the direction of pressure application.

Acknowledgments: This work was carried out under project "Developing of prospect materials for fabrication of alternative energy sources" in frameworks of "Prioritete-2030" program (No 20180174).

Synthesis and characterization of thermoelectric materials based on bismuth telluride doped with dysprosium

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The search for new and renewable energy sources is one of the most pressing problems of science and technology. To achieve a more large-scale development of environmentally friendly energy sources, it is necessary to carry out work on the development of new or modification of existing materials for such sources, including thermoelectric materials. There are several approaches to increasing ZT, based on the creation of a specific defective structure with the formation of impurity resonant levels that create the physical prerequisites for the manifestation of various spin effects (spin entropy, Kondo effect, spin transition states, etc.). These approaches can potentially be implemented by doping thermoelectric materials based on bismuth telluride with lanthanides.

In the field of study of thermoelectric materials based on bismuth telluride doped with lanthanides, methods for the synthesis of powdered materials (including nanomaterials) by reducing them from solution (solvothermal, hydrothermal, microwave synthesis, etc.) with their subsequent compacting by the method of spark plasma sintering (SPS) have become widespread. Each of the methods has a number of specific advantages: control of the shape and size of the particles of the initial powder, relatively short synthesis time, sintering time; all this together allows you to get volumetric materials with a given structure and a minimum grain size.

Thermoelectric materials $\text{Bi}_{2-x}\text{Dy}_x\text{Te}_{2.7}\text{Se}_{0.3}$ ($x=0; 0.001; 0.0025; 0.005; 0.005; 0.01$ and 0.02) were obtained by the method of solvothermal-microwave synthesis. The IPS method was used to compact the initial powdered materials. It was found that the resulting bulk materials are single-phase polycrystalline, with stoichiometric compositions in which an axial crystallographic texture is formed along the length directions $\langle 0\ 0\ 1 \rangle$ parallel to the direction of pressing. The concentration of the alloying element (Dy) affects the parameters of the crystal lattice, the average size of the synthesized particles and, as a result, the grain structure and the degree of texturing of bulk materials.

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Microstructure and thermoelectric properties of the cermet composites based on Bi_2Te_3 matrix with Ni@NiTe_2 inclusions

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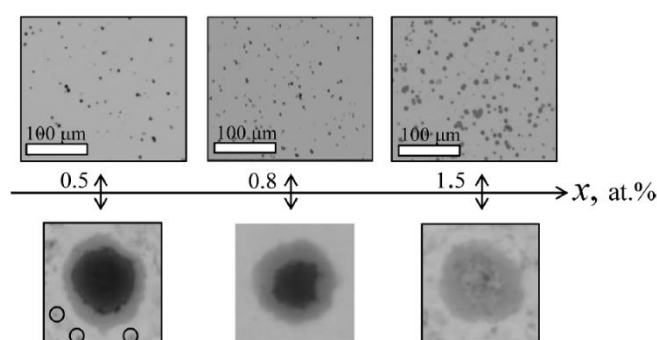
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One of promising approaches of modern thermoelectric materials science, which can result in remarkable enhancing thermoelectric efficiency of materials, is developing micro (nano) composites, which are based on a matrix of thermoelectric material with filler magnetic inclusions, randomly distributed inside the matrix [1].

Transmission electron microscope (TEM), X-ray diffraction (XRD) analysis, scanning electron microscopy (SEM) were applied. Thermoelectric properties of the composites were measured by using a ZEM-3 and TC-1200 system (a laser flash method) system.

Starting Bi_2Te_3 and Ni powders were spark-plasma-sintered (SPS) to prepare thermoelectric cermet composites consisting of thermoelectric Bi_2Te_3 matrix with different content, x , of ferromagnetic Ni filler ($x = 0.00, 0.50, 0.85, 1.25$ and 1.50 at. %). Grained Bi_2Te_3 matrix of composites is texturing under sintering. Texturing degree is x -dependent that is attributed to ability of Ni particles act as lubricant. New trigonal NiTe_2 phase is formed under SPS-process. The Ni and NiTe_2 phases correspond to filler Ni@NiTe_2 ("core"- "shell") inclusions (fig.1). Forming these inclusions is originated from chemical interaction between Bi_2Te_3 and Ni during SPS-process [2]. A $\text{Ni} \rightarrow \text{NiTe}_2$ reaction is accelerated with increasing x that results in growing Ni@NiTe_2 inclusions and increasing fraction of shell. Thermoelectric properties of composites are x -dependent that is due to non-monotonic changes in texturing degree, size of the inclusions and concentration of majority carriers with increasing x . Thermoelectric figure-of-merit of composites is remarkably enhancing as compared to that of Bi_2Te_3 matrix.

Fig. 1. Changing the filler Ni@NiTe_2 inclusions in the composites with increasing x . Top panel: BSE-images of surfaces for the composites with different x ; bottom panel: typical BSE-images of



the first, second and third type's inclusions.

[1] Zhao W., et al. "Magnetoelectric interaction and transport behaviours in magnetic nanocomposite thermoelectric materials." *Nature nanotechnology* 12.1 (2017): 55-60.

[2] Yaprıntsev M., et al. "Enhanced thermoelectric efficiency of the bulk composites consisting of "Bi₂Te₃ matrix" and "filler Ni@ NiTe₂ inclusions"." *Scripta Materialia* 194 (2021): 113710.

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Structural features of activating the shape memory effect of polylactide-based composite materials for medical applications

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The use of polymer materials opens up new opportunities for tissue engineering and medicine in general. The creation of composite materials can provide new properties for specific applications, but require more detailed study.

One of the most common polymers already used in medicine is polylactide (PLA). It has some already proven important characteristics, such as biocompatibility and biodegradation by hydrolysis, as well as less studied, but no less interesting properties, such as the shape memory effect. The shape memory effect (SME) of this polymer is a promising object of research, relevant for the creation of various adaptive medical structures and self-installing implants in the focus of reconstructive medicine.

The shape memory effect of polymers is a phenomenon in which a plastically deformed material transitions to its original shape when heated after deformation from a fixed temporary shape. The initial shape in thermally activated polymers with SME can be transformed into a temporary form by deformation at a fixed temperature above the transition temperature. Such a temperature for polylactide is the glass transition temperature when the mobility of the chain segments changes. Repeated heating above this temperature promotes transformation from a more ordered temporary configuration to a thermodynamically advantageous configuration with higher entropy. In a thermally activated polymer with SME, the coexistence of a hard phase and a soft phase is required, which determines the entropic elasticity of macromolecules and could be deformed into a temporary form.

The soft and hard phases are caused by the crystalline and amorphous structure of the base polymer. Accordingly, structural changes in the material will affect the activation of the shape memory effect. Structural modifications may be due to the incorporation of plasticizers (PCL) into the matrix, which increase the mobility of the matrix molecular chains, or functional particles, which most often act as centers of polymer crystallization, contributing to an increase in the crystallinity of the polymer base and, accordingly, the hard phase.

Another feature of activating the shape memory effect is a change in the structure of the polymer and plasticizer. This is especially clearly demonstrated for samples obtained by electrospinning. In this work, it was shown how the morphology of polymer scaffolds and the effects of recrystallization of various components of a polymer composite material change at various stages of the activation of the shape memory effect.

Shape memory composite material based on polylactide and CoFe_2O_4 nanoparticles for adaptive medical devices

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Adaptive medical devices (clips, staples) made of metal alloys with shape memory are currently used in surgery. However, metallic materials have some obvious disadvantages, such as limited restoring deformation (up to 10 %), possibility of overstressing, and lack of bioresorption capability. These limitations can be overcome by using alternative materials – shape memory polymers and composites based on them. The advantages of polymers are higher recoverable deformation values (more than 100 %), a possibility of shape memory effect activation temperature control (for instance, lowering it to 42 – 45 °C, acceptable for use in contact with a human body), mechanical and physicochemical characteristics. Another obvious advantage is the possibility of initiating the shape memory effect remotely, i.e. without direct thermal influence, e.g. by laser heating or influence of electric and magnetic fields. In the context of using such materials in the human body, induction heating (magnetic field exposure) of the polymer composite material with magnetic particles is advantageous, as this method eliminates traumatization of human tissues and acts only on the magnetic particles in the composite. Thus, polylactide-based composite material with magnetic particles, such as cobalt ferrite nanoparticles (CoFe_2O_4) [1], can be heated by applying a high-frequency alternating magnetic field.

In this work filaments of polylactide and cobalt ferrite composites (1, 5, 10 wt. %) were produced by extrusion. It was observed that the inclusion of dispersed filler affects the thermal properties and crystallinity of the polymer matrix. Samples of all three compositions show shape recovery after deformation. However, the sample containing 1 wt. % CoFe_2O_4 nanoparticles recovered the most rapidly. In addition, this composite material is non-toxic, so it can be used for biomedical applications.

The use of a polymer composite material based on polylactide with the possibility of indirect heating to activate the shape memory effect can thus solve the current problems associated with materials already existing and in use for this application.

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[1] Garanina A. S. et al. Temperature-controlled magnetic nanoparticles hyperthermia inhibits primary tumor growth and metastases dissemination // Nanomedicine: Nanotechnology, Biology and Medicine. – 2020. – T. 25. – C. 102171.

SCIS-2021

Posters

Patient organ doses from radionuclide therapy with ^{225}Ac -DOTATATE

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Targeted alpha therapy (TAT) is one of the promising cancer treatment methods in radionuclide therapy [Ошибка! Источник ссылки не найден.]. This approach reduces surgical intervention and is often the only way to preserve the function of the organ, for example, in the treatment of the prostate cancer. TAT is based on the delivery of alpha-emitting radionuclides to tumors for their therapy. A perspective alpha emitter for TAT today is ^{225}Ac , with a half-life of about 10 days, decaying in a cascade with the emission of 4 alpha particles, which significantly increases the radiobiological effect [2]. However, a negative consequence of TAT is concomitant irradiation of normal tissues. The organs of excretion, such as the kidneys and liver, where the radiopharmaceutical accumulates before being excreted from the body, are exposed to the highest dose. In this regard, a mandatory stage of treatment planning is the dosimetry modeling of TAT based on data on the bio-distribution of radionuclide in the patient body.

Due to the lack of data on the biodistribution of ^{225}Ac -DOTA-TATE in patient organs, its biodistribution was assessed using the acquired in SPECT study with ^{177}Lu -DOTA-TATE, considering the radiopharmaceutical does not depend on radionuclides and only a target molecule affects the biodistribution in the body. Since instability of the radiocompound, free ^{225}Ac release in the organs with other biodistribution. The calculation of its biodistribution was based on the modified compartment pharmacokinetic model from the Publication of ICRP 141 [3]. The biological distribution of daughter radionuclides was calculated as follows: for ultra-short-lived radionuclides ^{221}Fr and ^{217}At , the biodistribution was equated to the distribution of the parent ^{225}Ac ; for ^{213}Bi and ^{209}Pb , the models from the ICRP Publication 137 were used.

In this work, absorbed doses were determined in organs with the highest accumulation of ^{225}Ac -DOTE-TATE considering the instability of molecule and the redistribution of daughter radionuclides. High absorbed doses during the therapeutic procedure were estimated in the kidneys, liver and spleen. The released ^{225}Ac from the compound and its daughters made a significant contribution to the total dose (10%). The major part of absorbed dose was caused by alpha radiation, the contribution of photons and beta radiation were negligible small.

[1] G. Wang, R.M. de Kruijff, A. Rol et al., Appl Radiat Isot. 85,45-53 (2014).

[2] N.A. Thiele, J.J. Wilson, Cancer Biother Radiopharm.; 33 (8) (2018).

[3] F. Paquet, M.R. Bailey, R.W. Leggett et al., ICRP Publication 141: Occupational Intakes of Radionuclides: Part 4. Ann ICRP. (2019).

[4] F. Paquet, M. R. Bailey, R.W. Leggett et al, ICRP Publication 137: Occupational Intakes of Radionuclides: Part 3. Ann ICRP. (2017).

Influence of cold helium plasma treatment on PVDF film wettability and mesenchymal stem cell viability

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Fluorinated polymers are used as a base for magnetoelectric composites due to their high chemical inertness, thermal stability and electrical insulation properties [1]. Poly(vinylidene fluoride) (PVDF) is a fluoroplastic that has several crystal structures, of which the β -phase has the best piezo- and pyroelectric properties. The low surface energy of PVDF and its copolymers leads to high hydrophobicity and poor wettability of the polymer surface, which has a poor effect on cell adhesion to the substrate and limits their use in biomedical applications [2]. There are various methods for modifying PVDF surface (chemical etching, corona discharge treatment, plasma treatment, etc.), but the best in terms of biomedical applications is plasma treatment [3].

The main aim of this work was to investigate the effect of plasma treatment on the surface wettability of PVDF-based substrates and evaluate their biocompatibility on mesenchymal stem cell culture. The nanocomposites were fabricated by the doctor blade method and then treated with cold plasma. PVDF modified with a magnetic filler (CoFe_2O_4) was used as the substrate for the nanocomposites. The structural properties of the obtained samples were characterized using X-ray diffraction analysis (XRD). The wettability of the surface of the nanocomposites was investigated before and after plasma treatment by measuring the contact angle of the samples with water.

In this study, plasma treatment was shown to reduce the wettability angle and produce a more hydrophilic surface of the nanocomposites. A study on stem cells showed no significant reduction in viability (Fig.1), which in turn confirms the biocompatibility of the investigated nanocomposites and makes them interesting for biomedical applications.

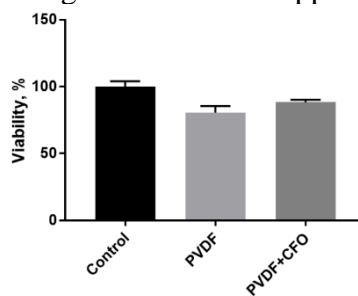


Figure 1: Viability of stem cells cultured on particle-free PVDF films (PVDF) and on composites based on PVDF modified with CoFe_2O_4 magnetic nanoparticles (PVDF+CFO).

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[1] D. Correia et al. Surface wettability modification of poly(vinylidene fluoride) and copolymer films and membranes by plasma treatment // Polymer. 2019

[2] D.M. Correia et al., Surface wettability modification of poly(vinylidene fluoride) and copolymer films and membranes by plasma treatment, Polymer, vol. 169, 138-147 (2019)

[3] Surface modification of polymers to enhance biocompatibility / M. Tavakoli // Surfaces and Interfaces for Biomaterials. 2005. P. 719-744

Structural studies of partially crystallized ferromagnetic micro-scale wires

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Anisotropic magnetic properties and miniature dimensions of ferromagnetic microwires make them promising materials for developing security control systems, coding devices and high performance sensors of low magnetic fields, mechanical stresses and temperatures for applications in microelectronics and bio-medical field [1–3]. Their magnetic, mechanical and structural properties can be tuned by various post-production annealing treatments and by varying the technological regime of preparation to suit particular applications. In this work, the structural properties of microwires produced by Taylor-Ulitovsky drawing and quenching technique are tuned by reducing the drawing speed in the air environment. This approach allows to control the extent of crystallization of microwires metallic nucleus, that defines their magnetic properties.

The magnetic microwires of three different compositions ($\text{Fe}_{77.5}\text{Si}_{7.5}\text{B}_{15}$, $\text{Fe}_{45}\text{Co}_{30}\text{Si}_{10}\text{B}_{15}$, $\text{Co}_{69}\text{Fe}_4\text{Cr}_4\text{Si}_{12}\text{B}_{11}$) and various drawing speeds were produced. The crystal structure (phase composition, crystal size, shape and orientation) of obtained microwires were studied by XRD and transmission electron microscopy (TEM). Depending on the drawing speed and chemical composition, the microstructure of the inner core is composed of the amorphous matrix with embedded nanocrystals.

The metallic core of Fe-rich microwires remained amorphous up to the smallest drawing speed.

While, FeCo-based microwires demonstrated partially crystallized structure. The amount of the crystallized phase increased with a decrease in the drawing speed and an increase in the nucleus diameter. TEM images reveal solitary round shaped polycrystalline regions in the cross section of the wires. The boundary of the crystallized and amorphous parts is clearly visible. The dark-field TEM images show elongated agglomerates, of grains with the close crystalline orientation, growing radially from the one center. In the Co-rich microwires, the amount and phase composition of the crystalline clusters also depended on the drawing speed, but in contrast to FeCo-based microwires, the clusters are more uniformly distributed over the microwire nucleus cross section.

The result of this work expands technological capabilities of Taylor-Ulitovsky manufacturing process and leads to the creation of novel way of tuning properties of ferromagnetic micro-scale wires through the dependence of the structural and magnetic characteristics on the drawing velocity.

References:

- [1] A. Uddin, et al, Compos. Part B. 176 (2019) 107190.
- [2] C. Morón, et al, Sensors (Switzerland). 15 (2015) 28340–28366.
- [3] S. Gudoshnikov, et al, Phys. Status Solidi Appl. Mater. Sci. 211 (2014) 980–985.

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UHMWPE-based bioactive materials for bone tissue regeneration

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Polymers are widely explored as materials for bone reconstruction. Ultra-high molecular weight polyethylene (UHMWPE) is a bioinert polymer which is used for bone and cartilage repair due to the biocompatibility, appropriate mechanical characteristics and low friction coefficient [1]. The incorporation of bioactive ceramic into polymer matrix leads to the enhanced bioactivity of the composite [2]. Bioactive composite materials are the promising candidates for bone tissue defects repair.

The most studied bioactive filler is hydroxyapatite, the calcium phosphate bioceramic. The UHMWPE/hydroxyapatite composites have demonstrated the possibility to be used as bone substituting materials [3]. Current work studies the manufacturing of UHMWPE/diopside composite material.

Diopside ($\text{CaMgSi}_2\text{O}_6$) is a silicate bioactive ceramic, demonstrating the bioactivity via apatite formation during incubation in SBF [4]. Diopside was synthesized by sol-gel combustion method using glycine as a fuel [5]. Diopside precursor was calcined at different temperatures for 0, 2, 4, and 6 hours, the obtained powder was analyzed by XRD using a DRON diffractometer with Co K α radiation source ($\lambda = 1.7902 \text{ \AA}$). Particle size was measured using SEM by means of VEGA3 TESCAN.

Diopside particles with a mean size of ~200 nm and UHMWPE powder were mechanically activated, mixed with salt, and subsequently hot molded at 190°C. Salt-containing hot molded samples were washed with distilled water until complete salt removal.

Prepared UHMWPE-based porous materials were investigated using SEM, the structural characteristics and porosity were evaluated using ImageJ software.

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[1] M. A. Mateos-Timoneda, Woodhead Publishing. 231-251 (2009)

[2] M. Zhang, Journal of SCS. 26, 101470 (2022)

[3] F. Senatov, MS&E: C. 111, 110750 (2020)

[4] R. Choudhary, MS&E: C. 118, 111456 (2021)

[5] R. Choudhary, Journal of ACS. 8, 1051-1065 (2020)

3D-printed TPU scaffolds filled with agar for ear reconstruction

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Introduction

A common pathology of the maxillofacial region are various defects and deformities of the external ear. We should note that there is a tendency to increase the number of patients with this problem [1]. The auricle is an important distinguishing feature of the human face and, therefore, its deformation has a profound effect on self-confidence in both adults and children [2]. That is why the reconstruction of the auricle is an important mission among scientists.

Methods

We obtained an agar-agar-based hydrogel by cryotropic gelation. For a hydrogel crosslinked with ferulic acid, we crosslinked a solution of agar-agar with ferulic acid at 60°C for 3 hours. We printed porous scaffolds with various degrees of filling based on TPU using a modified Prusa i3 Pro (Geeetech, China). The pores had a gyroid structure. We built them manually.

We tested samples using Universal testing machine ProLine Z020 TN (ZwickRoell, Germany). Samples were evaluated in tension and compression. We also carried out thermogravimetric analysis using thermogravimetric analyzer SDT Q50 (TA Instruments, USA). We evaluated the cytotoxicity of samples by incubating tooth MMSCs with sample extracts for 24 and 96 hours.

Results

Hydrogel samples based on agar-agar with concentrations from 1% to 5% showed Young's modulus of tensile from 32.5 ± 4.1 kPa to 191.4 ± 24.0 kPa, tensile strength from 17.2 ± 4.4 kPa to 59.6 ± 13.2 kPa. We chose the concentration of 3.5% as the most technologically advanced.

We conducted a study of the mechanical properties of a hydrogel based on agar-agar cross-linked with ferulic acid, the degree of cross-linking is 0.1 mol/mol. Young's modulus in tension was 99.1 ± 7.5 kPa, ultimate strength 0.9 ± 0.1 kPa, elongation at break $38.4 \pm 1.5\%$.

Using thermogravimetric analysis, we determined the optimal temperature range for the operation of hydrogel forms from agar-agar. It ranged from 0°C to 110°C.

Using the results of the study of the hydrogel dissolution kinetics, we confirmed its stability (the dissolution coefficient does not exceed 10%)

We have tested porous TPU scaffolds with fill rates from 10% to 100% for compression. For a degree of filling of 15% Young's modulus was 1.6 ± 0.23 MPa, the ultimate strength was 0.097 ± 0.003 MPa. This corresponds to the mechanical properties of native cartilage.

The viability of the tooth MMSC after incubation with sample extracts ranged from 85% to 100%, which indicates the non-toxicity of the samples.

References

- [1] Безруков В. М., Робустова Т. Г. (ред.). Руководство по хирургической стоматологии и челюстно-лицевой хирургии. – Медицина, 2000.
- [2] Zhou G. et al. In vitro regeneration of patient-specific ear-shaped cartilage and its first clinical application for auricular reconstruction //EBioMedicine. – 2018. – Т.28. – С. 287-302.

Deformation of quasi-stable configurations of magnetically active elastomers in a 2D formulation

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In the last few years, there has been an increased interest in “smart” materials based on a polymer with magnetic inclusions [1, 2]. Numerical methods are used to study the quantitative properties of such materials [3, 4]. This work is devoted to the calculation of deformations in an external field of a structured magnetically active elastomer with magnetically hard inclusions in a 2D formulation by the finite element method using the FEniCS package.

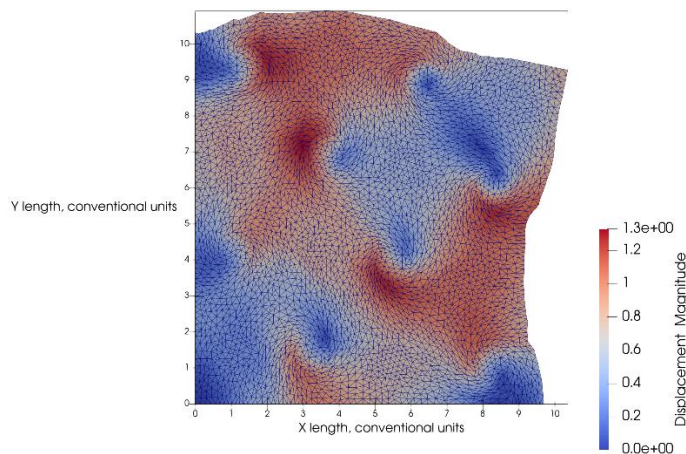


Figure 1 - Deformation of an elastic matrix with magnetically hard particles in an external magnetic field.

In the initial state, the particles (Fig. 1) were located at the nodes of a 4 by 4 rectangular grid with square cells and had arbitrarily oriented magnetic moments.

To describe the matrix, the model of a hyperelastic material with the Neo-Hooke potential was used [5]. The magnetic particles were single-domain and had the shape of an ideal circle. The model assumes complete adhesion of particles and matrix, i.e. the possibility of separating the matrix from the particle was excluded.

As a result, the deformations of the material were calculated depending on the initial orientation of the magnetization of the particles and the magnitude of their magnetic moments.

- [1] Allue, A., Corte-León, P., Gondra, K., Zhukova, V., Ipatov, M., Maria Blanco, J., Zhukov, A. (2019). Smart composites with embedded magnetic microwire inclusions allowing non-contact stresses and temperature monitoring. *Composites Part A: Applied Science and Manufacturing*.
- [2] Omelyanchik, A.; Antipova, V.; Gritsenko, C.; Kolesnikova, V.; Murzin, D.; Han, Y.; Turutin, A.V.; Kubasov, I.V.; Kislyuk, A.M.; Ilina, T.S.; et al. Boosting Magnetoelectric Effect in Polymer-Based Nanocomposites. *Nanomaterials* 2021, 11, 1154.
- [3] Germain Sossou, Frédéric Demoly, Hadrien Belkebir, H. Jerry Qi, Samuel Gomes, Ghislain Montavon, Design for 4D printing: Modeling and computation of smart materials distributions, *Materials and Design*, 181 (2019) 108074.
- [4] O.V. Stolbov, Yu.L. Raikhera and M. Balasoiubc. Modelling of magnetodipolar striction in soft magnetic elastomers. *Soft Matter*, 2011, 7, 8484
- [5] Лурье А.И. Теория упругости, Наука, 1970.

Magnetoelectric effect modelling in magnetoactive elastomers

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Magnetoelectric effect (MEE) – is an effect of change of electrical polarization of the material under magnetic field:

$$\Delta P = P(E)_H - P(E)_0$$

This effect is often observed in multiferroics as a result of the interaction of electrical and magnetic subsystems. And it has been of great interest in recent years because of the possibilities of using it in a wide range of areas, such as development of electromagnetic field detectors or energy conservation and conversion [1].

The strongest magnetoelectric effect is manifested in composite multiferroics [2]. Polymer multiferroics are of particular interest due to the possibility of their application in flexible electronics and biomedicine [3]. A well-known representative of this class of multiferroics are magnetoactive elastomers (MAE). The presence of a magnetoelectric effect in a composite based on a MAE was previously experimentally shown [4].

In this work we present the results of numerical modelling of MEE in MAE. Model is based on the assumption about the displacement of ferromagnetic (FM) and ferroelectric (FE) particles inside the elastic matrix under the external magnetic field and the formation of chain-like structures.

To calculate particles positions, the Verlet integration [5] was used. We considered dipole-dipole model for particle-particle interaction and “springs” model [6] for particle-matrix elastic interaction.

We consider systems varying concentration of FM and FE fillers, size and space distribution of particles, elastic properties of the matrix. For simulation of the presented model and visualization of the system tool was designed using C++ and Python programming languages.

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- [1] Spaldin N. and Ramesh R. *Nat. Mater.* 2019
- [2] Jianq Q. et. al. *J. Am. Ceram. Soc.* 2011
- [3] Omelyanchik A. et. al. *Nanomaterials* 2021
- [4] Makarova L. et.al. *JMMM* 2019
- [5] Verlet, L. *Phys. Rev.* 1967

Magnetoactive elastomers based on ferromagnetic and ferroelectric particles: A FORC approach

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Magnetic and structural properties of composites based on ferromagnetic microparticles or a mixture of ferromagnetic (FM) and ferroelectric (FE) microparticles embedded into a soft polymer matrix were studied and compared. This class of materials belongs to magnetoactive elastomers (MAE) which received renewed interest stimulated by breakthroughs in their applications, for example, in soft robots and biomedical technologies. Moreover, the MAE with a mixture of ferromagnetic and ferroelectric particles exhibit multiferroic properties which open new ways for their application. In this work, the elastomer with the mixture of FM and FE microparticles inside the soft polymer matrix (with Young's modulus <1 MPa) was studied and compared with composites, containing only FM particles of different concentrations. It was shown earlier experimentally [1,2] and numerically [3] that such elastomers exhibit multiferroic properties, namely, the change of magnetic properties under the external electric field and vice versa. We investigated the structural properties of MAE with different compositions by high-resolution X-ray computer tomography (XCT), X-ray diffraction (XRD) and scanning electron microscopy (SEM) with energy dispersive X-ray (EDX) analysis. Magnetic properties of obtained composites were studied by vibrating-sample magnetometry (VSM) employing the method of FORC analysis to distinguish the effects of magnetization reversal processes, occurring due to the magnetization switching and particle movement mechanisms correlated with effects of magnetic interparticle interactions. The influence of FE particles on the local switching fields and interaction fields of the MAE was observed by FORC analysis.

The non-magnetic components added to the MAE indirectly modulate its magnetic properties by changing the elastic properties of the polymer matrix and affecting the magnetic interparticle interactions, which were observed in the FORC diagram. The effect of the non-magnetic phase on magnetic interparticle interactions occurs by modulation of the spatial distribution of FM particles, where the non-magnetic phase acts as an excluding volume. MAE with the mixture of FE and FM particles is an example of flexible multiferroics that can be used in engineering and biomedical areas.

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References:

- [1] Makarova, Liudmila A., et al. "New Multiferroic Composite Materials Consisting of Ferromagnetic, Ferroelectric, and Polymer Components." *IEEE Transactions on Magnetics* 53.11 (2017).
- [2] Makarova, Liudmila A., et al. "Multiferroic Coupling of Ferromagnetic and Ferroelectric Particles through Elastic Polymers." *Polymers* 14.1 (2022): 153.

Spinal cages based on auxetic metamaterial: CAD design concept, 3D printing and mechanical testing

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Auxetic metamaterials are characterized by a negative Poisson's ratio and exhibit properties of all-round expansion under tension and compression compaction. Such properties can be achieved by constructing special geometrical structures, which can be fabricated from different materials and by different methods. Since the properties of metamaterials are determined more by geometry than by materials and manufacturing methods, this provides an opportunity to optimize the biomechanical characteristics of medical devices for the spinal column. The development of medical devices to compensate for spinal column defects remains a pressing problem in modern spine surgery. Current surgical solutions used for intervertebral disc reconstruction include artificial discs and interbody spinal cages. According to clinical studies, complete cage failure was observed in 5% of cases due to the «stress shielding» effect. To address the identified problems, the field of spinal surgery has evolved to adapt existing interbody cages in the form of porous or auxetic products. Optimization of mechanical characteristics of auxetic for example can be achieved by adjusting the geometry of the cell. The geometry forming the auxetic metamaterials can play an important role in varying the mechanical properties of spinal interbody cages, potentially reducing stress shielding effects and increasing product life.

The first aim of the research is to optimize interbody box-shape cage by integrating auxetic and honeycomb structures using standard CAD functions. Second aim of the research is to analyze the mechanical properties by static compression of the experimental cages obtained by 3D printing using Ti-6Al-4V powder and comparison with the characteristics of the bone tissue to investigate the potential reduction in the effect of stress shielding.

The results of static compression tests (up to 15 kN, which is 2.5 times the maximum vertebra load) showed that the honeycomb structure has the lowest mechanical characteristics. The accelerated accumulation of longitudinal strain in honeycomb cage results in the lowest Young's modulus value compared to other specimen types of 1.19 ± 0.03 GPa. Nevertheless, the mechanical characteristics of the honeycomb structure were close to mechanical characteristics of trabecular bone ($E = 0.043\text{--}0.165$ GPa) and vertebra ($E = 0.374$ GPa). Complete failure of honeycomb cage was observed at stress 21.13 ± 6.33 MPa. The auxetic cage showed the second highest mechanical characteristics. Cage with auxetic configurations under compressive loading slowed the accumulation of longitudinal deformations and increased the stiffness of the cage by ~6 times that of the honeycomb ($E = 6.68 \pm 0.28$ GPa). The result is an auxetic that is similar in mechanical properties to that of cortical bone ($E = 7\text{--}30$ GPa) and revealed no visible failure of the metamaterial structure. Finally, the box-shaped cage showed the highest strength characteristics ($E = 11.78 \pm 0.26$ GPa) and at a maximum force of 15 kN, box-shape cage is still in the elastic region. The results of mechanical tests are presumably explained by the value of the slope angle between the ribs of the honeycomb (auxetic) structure. The position of the ribs at an angle of more than 90 degrees leads to an accelerated accumulation of longitudinal deformation and premature failure of the specimens. Accordingly, the placement of the ribs at an angle of less than 90 degrees resulted in a decrease longitudinal strain and, as a consequence, an increase in the stiffness of the specimens

Sorption of copper(II) ions on multilayer $\text{Ti}_3\text{C}_2\text{T}_x$ MXenes

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Heavy metals are a major cause of environmental pollution due to their non-degradable and persistent nature in the environment; these elements are considered very dangerous even at low concentrations.

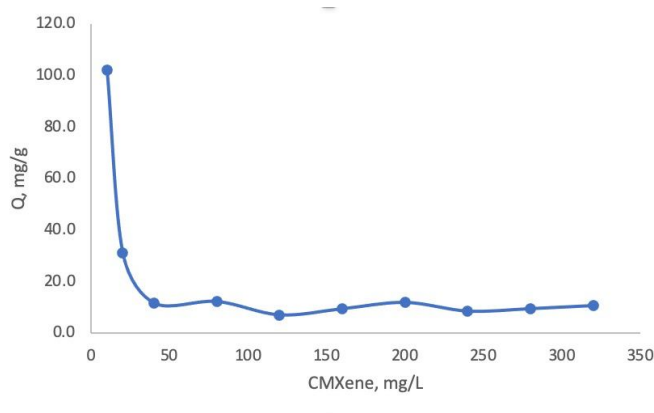
Copper (Cu), a potentially toxic heavy metal, must be removed from sewage and drinking water because short- and long-term acute exposure causes food poisoning, gastrointestinal illness, nausea, and disruption of homeostasis in the human liver. Acceptable limits for Cu are 1.5 mg/L in drinking water and 1.3 mg/L in industrial waste, according to the World Health Organization (WHO) and the US Environmental Protection Agency, respectively. Therefore, the presence of Cu in water above the specified limit must be eliminated. A number of methods are used to remove copper and other heavy metals from water and wastewater, such as ion exchange, chemical precipitation, membrane filtration, flocculation and/or coagulation and adsorption.

Among the available technologies, adsorption is a simple and economical method, since it does not require additional processing after removal of copper ions from the matrix.

In recent years, the development of micro- and nanomaterials and their application in Cu adsorption has been widely discussed. These materials have become effective adsorbents for copper and other heavy metals in wastewater treatment due to their unique and high adsorption capacity.

MXenes are a new family of 2D transition metal carbide nanosheets similar to graphene. Some transition metal carbides have been prepared by selective etching of certain elements from hexagonal MAX phases by aqueous and non-aqueous methods. MAX-phases ($\text{M}_{n+1}\text{AX}_n$; $n = 1, 2$ or 3) are ternary carbides and nitrides, consisting of early transition metals (M), elements of groups IIIA and IVA (A) and a carbon and/or nitrogen component (X). Due to their unique structural, electrical and chemical properties, they are used in many applications such as energy storage, chemical sensors, catalysts and supercapacitors.

In this work, MXenes are synthesized and their sorption properties for copper (II) ions are studied.



Dependence of the capacitance of maxenes on their concentration

This research was financially supported by the Russian Scientific Foundation, Project number 22-12-20036.

Study of the Effect of Filling Thermoplastic Medical Polyurethane with PVA, PLA or Diatomite on the Relaxation Times Distributions of ^1H NMR

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In this work, to characterize the mobility of different sections of the macromolecules of polyurethane (PUR), polyvinyl alcohol (PVA), and polylactic acid (PLA), as well as the density of crosslinks of the polymer chains when using fillers, we used the distributions of spin–lattice and spin–spin relaxation times for the protons. It is shown that the rigidity of the thermoplastic polymers depends on the sizes of the granules of the diatomite filler, which can embed in the polymer matrix. Consequently, relaxation times are reduced. If PLA is the filler of PUR, the dynamics of the molecules in the chains and the spin–spin interaction of the protons are affected by the crosslinking of PUR by PLA. An increase in crosslinks density reduces the rate of polymer degradation [1].

NMR relaxation measurements were done at 300MHz proton frequency with a 7T superconducting magnet and a helium bath cryostat. The investigated filaments for 3D-printing were studied in a post-extrusion state. MAS method was not used in the work. Solid polymers can be prepared for MAS NMR measurements in two ways: either precisely machining the suitable sample insert for the MAS rotor from the bulk polymer or grinding the sample into the fine powder. The first way was not applicable in our case, because the polymerization of the samples occurs during the extrusion process, and the samples have the form of filaments. Grinding the samples into a fine powder was not desirable, because this would lead to a size effect influence on the relaxation times and to the mechanical destruction of polymer crosslinks. In this regard, the measurements were performed statically.

To study the effect of filler on the mobility of fragments of polymer macromolecules, on the density of chain crosslinks, and on the modification of polymer properties for 3D printing, we used the distribution of NMR relaxation times of hydrogen nuclei. It is assumed that the influence of the diatomite filler on the rigidity of thermoplastic polymers for the FDM 3D printing of scaffolds depends on the size of the filler granules that can embed in the polymer matrix. This leads to a reduction of relaxation times. When for PUR is used as a PLA filler, the dynamics of molecules in chains and the spin–spin interaction of protons are affected by crosslinking of PUR via PLA. [2] The addition of PVA to polyurethane has practically no effect on the relaxation times distribution, since the composite material obtained from the melt using a twin-screw extruder is a simple mixture of two polymers and there is no crosslinking of PUR by PVA.

This study can help to expand the range of methods for controlling the properties of medical polymers suitable for the manufacture of filaments for FDM 3D-printers. The use of the above polymers allows to obtain biocompatible structures with different properties for use in various fields of medicine.

[1] J. Kucińska-Lipka, *Materials* 11, 352 (2018).

[2] J. Brzeska et al., *Int. J. Polym. Sci.* (2015).

Magnetic properties of 2D permalloy-based magnetoplasmonic crystals for sensing applications

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Combination of plasmonic and magnetic materials in magnetoplasmonic crystals (MPICs) for excitation of magneto-optical surface plasmonic resonances [1] can be used for the effective magnetic field [2] or biomedical sensing [3]. Common configurations of MPICs are based on the 1D diffraction gratings sensitive to one direction of an external magnetic field. For simultaneous detection of several components of the magnetic field one can use 2D MPICs. However, such structures have complex magnetic properties depending on their parameters and composition. This work is devoted to the study of magnetic properties of a series of 2D permalloy-based MPICs for sensing applications depending on the electron beam direct writing dose used for the preparation of the structures.

Substrates with two-dimensional diffraction gratings (period $d = 610 \pm 20$ nm and height $h = 80 - 90$ nm) for MPICs fabrication were made by the electron beam lithography method. The electron beam direct writing was performed with the doses of 200, 250, 300, 350, 400, 450, 500, 550 and 600 $\mu\text{C}/\text{cm}^2$. MPICs were made by the magnetron sputtering method to form a three-layered structure of the Ag (100 nm)/Ni₈₀Fe₂₀ (70 nm)/Si₃N₄ (15 nm) on top of the fabricated substrates. Magnetic properties of the MPICs were studied with the EvicoMagnetics GmbH Magneto-optical Kerr microscope in two orthogonal directions of the magnetic field. Examples of the obtained hysteresis loops and a Kerr-microscopy image are shown in the Fig. 1.

To conclude, it is shown that studied samples' coercive field strongly depends on the direction of the applied magnetic field and has non linear dependance on the used electron beam direct writing dose. The results will be used in future studies to explain magneto-optical properties of the 2D MPICs.

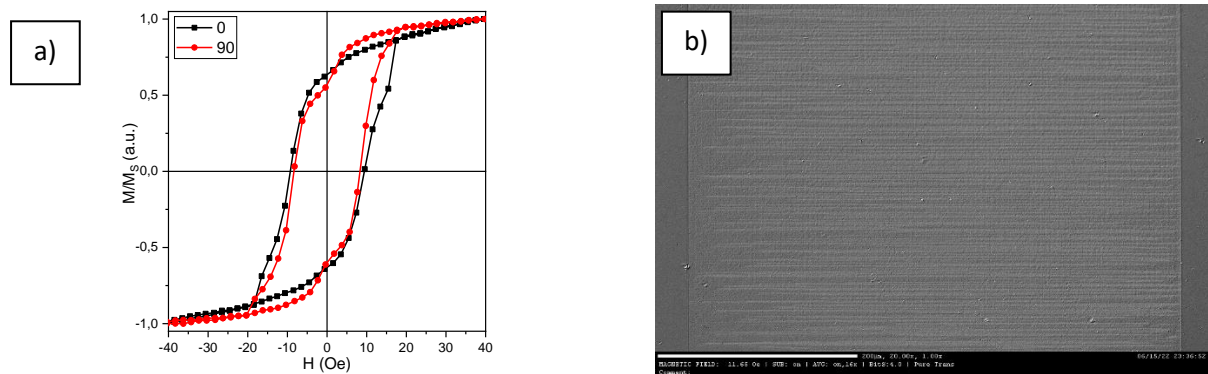


Fig. 1. (a) Hysteresis loops obtained in two orthogonal magnetization directions of the sample with the electron beam direct writing dose of 250 $\mu\text{C}/\text{cm}^2$. (b) An example of the Kerr-microscopy image of the sample with the electron beam direct writing dose of 250 $\mu\text{C}/\text{cm}^2$ in the external magnetic field of 11.64 Oe. Scale bar is 200 μm .

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[1] Rizal, C.: IEEE Transactions on Magnetics, 57(2), 1-5 (2020).

[2] Belyaev, V.K.: Scientific Reports, 10(1), 1-6 (2020).

[3] Chandra, S.: ACS Photonics, 8(5), 1316-1323 (2021).

Structure, physico-mechanical properties and piezoelectric response of electrospun composite magnetic PHB/Fe₃O₄-rGO scaffolds with different fiber diameters

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In this study, the effect of hybrid magnetic Fe₃O₄-rGO filler and fiber diameter on the structure, mechanical, magnetic and piezoelectric properties of PHB scaffolds has been studied. Fe₃O₄/rGO composite with a high saturation magnetization 96.27 ± 1.42 emu/g has been synthesized through *in-situ* co-precipitation method. Defect-free pure and composite PHB scaffolds has been successfully fabricated *via* electrospinning with fiber diameters of 1.6 ± 0.3 μm and 2.4 ± 0.5 μm for pure PHB scaffolds, and 1.7 ± 0.3 μm and 3.0 ± 0.5 μm for composite PHB/Fe₃O₄-rGO scaffolds.

A decrease in the fiber diameter and addition of Fe₃O₄-rGO filler result in the decreased crystallinity of the scaffolds. The decrease of fiber diameter enhances elongation at break and ultimate tensile stress of the electrospun scaffolds. The elongation at break increases from 10 ± 1.5 to 15 ± 3.0 % for pure PHB scaffolds and from 7.8 ± 2.6 to 18.5 ± 5.7 % for PHB/Fe₃O₄-rGO composite scaffolds. The enhanced ductility of finer fibers is associated with higher ability of such fibers to absorb a considerable amount of energy before failure. Thinner fibers with diameters of 1.6 ± 0.3 and 1.7 ± 0.3 μm possess ultimate strength values of 2.50 ± 0.27 and 1.05 ± 0.18 MPa for pure and composite scaffolds, respectively, which are more than twice higher than those of scaffolds with fiber diameters of 2.4 ± 0.5 and 3.0 ± 0.5 μm . Elongation at break slightly increases after the addition of Fe₃O₄-rGO composite fillers from 15.0 ± 3.0 to 18.5 ± 5.7 %. However, the addition of Fe₃O₄-rGO fillers results in the decrease of ultimate strength from 1.35 ± 0.10 to 0.49 ± 0.15 MPa and from 2.50 ± 0.27 to 1.05 ± 0.18 MPa for scaffolds with thick and thin fibers, respectively. Moreover, Young's moduli are lower as well in the composite scaffolds compared to that of pure ones.

Surface electric potential of the magnetoactive PHB/Fe₃O₄-rGO composite scaffolds significantly increases from 0.650 ± 0.012 to 0.890 ± 0.034 V with increasing fiber diameter due to a higher amount of the polar functional surface groups. There is no effect of different microfiber size on both the effective local out-of-plane and in-plane piezoresponses for the hybrid magnetic PHB fibers. At the same time, the developed scaffolds possess high saturation magnetization 6.50 ± 0.39 and 6.83 ± 0.41 emu/g for scaffolds with 2.4 ± 0.5 and 3.0 ± 0.5 μm fibers, respectively.

Thus, the addition of magnetic Fe₃O₄-rGO composite filler into PHB scaffolds does not affect the piezoresponse of scaffolds, however, provides pronounced magnetic properties. In addition, the ductility, tensile strength and surface electric potential of the magnetoactive electrospun PHB/Fe₃O₄-rGO scaffolds can be controlled by varying the fiber diameter. Thus, the developed PHB/Fe₃O₄-rGO scaffolds, which are able to provide external mechanical and electrical stimuli, are promising candidates for bone tissue engineering.

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Fabrication and study of the properties of ferromagnetic nanoparticles based on silver-containing nickel-zinc ferrites for wastewater treatment

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In recent years, many countries in the world began to pay close attention to the ecology of our planet, due to which the importance of reducing environmental pollution, including wastewater treatment in urban areas, is an urgent issue. There are several effective methods of water purification [1], such as adsorption, ion exchange, membrane filtration [2], water ozonation and electrochemical method for decentralized water treatment systems [3]. However, these methods have varying degrees of effectiveness, depending on where they are used, purpose and economic viability. The development of new, efficient and easy-to-use treatment will contribute to solving the environmental problem.

Metal-containing nanoparticles (Fe, Zn, Ag, Ni, etc.) are a promising tool for wastewater treatment due to properties such as low production cost, chemical disinfection, high adsorption activity of particles and the ability to chemical degradation, which ensures the efficiency of industrial wastewater and drinking water treatment [1-2].

In this work, we propose to use a solution that will combine the biological and chemical (adsorption) activities of each of the above-described elements in one material - nanoparticles of chemical composition $\text{AgXNiYZnZFe}_2\text{O}_4$, where $X \leq 0.05$, and $Y+Z=1-X$, which will have magnetic properties, which will allow to easily collect this nanomaterial after water treatment using a gradient magnetic field. Silver has antibacterial properties, which allows capturing viruses and bacteria at the stage of biological purification from organic pollutants, preventing them from penetrating into pure water. The surface properties of nanoparticles, their activity as an absorbent of heavy metals and antibacterial action, have a decisive influence as they affect both chemical (passivation, dissolution, etc.) and physical (adhesiveness to the bacterial membrane, aggregation, etc.) properties.

The results of silver-containing $\text{AgXNiYZnZFe}_2\text{O}_4$ nanoparticles synthesized by co-precipitation with and without the addition of FeCl_2 salt are presented. The diffraction patterns of nanoparticles were obtained using an X-ray powder diffractometer (XRD). The homogeneity of element distribution in the samples was examined using a scanning electron microscope (SEM) with an energy dispersive X-ray (EDX) analyzer. The magnetic properties of samples were studied on a vibrating sample magnetometer (VSM).

Thus, based on the analysis of the results obtained, the optimal synthesis parameters were determined and a method of manufacturing nanoparticles with the composition of $\text{AgXNiYZnZFe}_2\text{O}_4$ was optimized. In the future, taking into account the results obtained, it is planned to production nanoparticles by sol-gel self-combustion method and study their properties with subsequent biological examination to evaluate the cytotoxicity of the obtained nanoparticles.

The study was supported by the Russian Science Foundation under Grant No. 22-22-20124.

[1] Zhe Xu, et al. A critical review on chemical analysis of heavy metal complexes in water/wastewater and the mechanism of treatment methods. *Chemical Engineering Journal*. 429 (2022) 131688.

[2] N. Abdullah, et al. Recent trends of heavy metal removal from water/wastewater by membrane technologies, *J. Ind. Eng. Chem.* 76 (2019) 17–38.

[3] S. Garcia-Segura, et al. Opportunities for nanotechnology to enhance electrochemical treatment of pollutants in potable water and industrial wastewater-a perspective, *Environ. Sci. Nano.* 7 (2020) 2178–2194.

[4] Savage N., Diallo M. S. Nanomaterials and water purification: opportunities and challenges // *Journal of Nanoparticle research*. – 2005. – T. 7. – №. 4-5. – C. 331-342.

[5] Auffan M. et al. Towards a definition of inorganic nanoparticles from an environmental, health and safety perspective// *Nature nanotechnology*. – 2009. – T. 4. – №. 10. – C. 634.

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