IV INTERNATIONAL CONFERENCE

Nanobiophysics 2015:
Fundamental and Applied Aspects

To the memory of Prof. Valery Kharkyanen

1 - 4 October 2015,
Kyiv, Ukraine

BOOK OF ABSTRACTS

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BOOK OF ABSTRACTS

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- Verkin Institute for Low temperature Physics and Engineering of the National Academy of Sciences of Ukraine

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To the memory of Valery M. Kharkyanen

Prof. Valery M. Kharkyanen, an outstanding researcher and the organizer of science, head of Department of Physics of Biological Systems of the Institute of Physics of NAS of Ukraine, passed away on August 1st 2013 at the age of 68.

Prof. Kharkyanen was a bright representative of the famous school of theoretical physics established by Prof. A.S. Davydov. His scientific career started in 1970 in the Institute of Theoretical Physics in Kiev from the studies of antiferroelectrics, spin-orbital ordering in crystals and other quantum phenomena. After defending his PhD and till the end of life he was investigating the mechanism of functioning of biological macromolecules in non-equilibrium conditions.

At the end of seventies real structure were known for very few complex biological objects and the nature of their dynamical and conformational properties were mysterious. The most promising from the theoretical point of view was the study of the donor-acceptor electron transfer in proteins, which could be described by means quantum tunneling and classical activation kinetics without consideration of real molecular structure. At that time Prof. Kharkyanen started working with the reaction centers of photosynthetic bacteria, which were ideal object for studying electron transfer phenomena.

In 1983 Prof. Kharkyanen formulated the idea of dynamic structural self-organization in proteins in non-equilibrium conditions. The concept was extremely simple and elegant – fast charge transfer reactions in the active site of the protein leads to the polarization of the protein globule with long relaxation times. Polarization triggers conformational transitions in the globule, which, in turn, change the effective free energy potential of the charge transfer reactions. The system becomes self-organized and could exhibit many non-trivial synergetic effects, such as hysteresis and emergence of new non-equilibrium steady states [1]. These ideas were later applied to bacterial photoreaction centers [2], ion channels [3], enzymes and other objects [4].

In 1989 V.M. Kharkyanen obtained the degree of the Doctor of Science in theoretical physics for the studies of kinetic theory of the charge transfer in biomolecular systems. In 1991 his group started long-term dedicated experimental studies of bacterial photoreaction centers, which were designed to prove the existence of the self-organization phenomena. The predictions of the theory were confirmed brilliantly [1, 2, 5-7]. These works are the prominent example of the state-of-the-art complementarity between the theoretical and experimental studies. Prof. Kharkyanen continued this line of reserches till the end of his life.

Starting from the end of nineties the focus of recherches of Prof. Kharkyanen gradually shifted toward using real 3D structure of proteins in combination with theoretical studies. During the years he was intrigued by the complex process of multi-particle ionic diffusion in the ion channels. The structure of the ion channel inspired him and co-authors to develop the general theory of multi-particle diffusion in the narrow pores. Before his work this fundamental problem of statistical physics remained unsolved. In 2010 the general theory of the single-file multi-particle diffusion was completed [8, 9]. It was widely recognized as the valuable contribution to fundamental statistical physics and theoretical biophysics.

At the same time advances in numerical simulations allowed applying the concept of dynamic self-organization to KcsA ion channel with known structure. In the series of works the real structure of this channel was used to build the model of its activation kinetics and to show, that the self-organization phenomena are possible in this particular channel [10, 11]. Despite the elegant and convincing application of the theory, these works are still not properly appreciated by the community.

In the last years of his life Prof. Kharkyanen was interested in the problem of signal processing in the single-molecule biophysical experiments. His idea was to extract as much information as possible about internal kinetics from the sequence of events, recorded from the single macromolecule. He proposed an elegant theory of processing such signals based on the decomposition of its autocorrelation functions. His last research paper, based on these results, was accepted next day after he tragically passed away.

The science was the sense of life for Valery Kharkyanen. His colleagues, collaborators and students were always inspired and motivated by his creativity, positive thinking and exceptionally deep understanding of the physics. His charisma and personal qualities allowed him creating an extremely friendly and productive environment in the department of physics of biological systems of the Institute of physics of NASU. His ideas will continue to guide future researches of the department and inspire the researches working in the area of theoretical biophysics worldwide.

The memory of Valery Kharkyanen will always be in our hearts.

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2. Gushcha, A.O., et al., *New physical phenomenon of dynamic self-organization in molecular electron transfer systems.* . Phys. Lett. A., 1994. **191**: p. 393-397.
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4. Christophorov, L.N. and V.N. Kharkyanen, *Synergetic mechanisms of structural regulation of the electron transfer and other reactions of biological macromolecules.* Chemical Physics, 2005. **319**: p. 330-341.
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7. Goushcha, A.O., et al., *Self-regulation phenomena in bacterial reaction centers. I. General theory.* Biophys J, 2000. **79**(3): p. 1237-52.
8. Kharkyanen, V.N. and S.O. Yesylevskyy, *The theory of the single-file multi-particle diffusion in narrow pores* Phys. Rev. E, 2009. **80**: p. 031118.
9. Kharkyanen, V.N., S.O. Yesylevskyy, and N.M. Berezetskaya, *Approximation of super-ions for single-file diffusion of multiple ions through narrow pores.* Physical Review E, 2010. **82**(5): p. 051103.
10. Kharkyanen, V.N., et al., *Semi-quantitative model of the gating of KcsA ion channel. I. Geometry and energetics of the gating.* . Biopolymers and Cell, 2009. **25**(5): p. 390-397.
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Department of Physics of Biological Systems

The department of physics of biological systems was created in the Institute of Physics in 1995 for studying the biological objects by the methods of theoretical and experimental physics. The department was founded by the famous theoretical physicist **Prof. Valery Kharkyanen** (28.06.1946 — 01.08.2013).

The physical principles of functioning of the biological macromolecules and their assemblies are studied by the combination of experimental, theoretical and computational methods. Experimental techniques include various methods of the surface-enhanced infrared and Raman spectroscopy. Theoretical studies are focused on slow conformational dynamics, stochastic dynamics and the phenomena of dynamic self-organization. Computational techniques involve quantum chemistry and atomistic and coarse-grained molecular dynamics simulations. Data analysis techniques and innovative molecular modeling software are also developed.

Experimental facilities

Spectrophotometer with diffuse reflectance attachment (UV-260 Shimadzu), IR Fourier spectrometer Bruker IFS-66, surface plasmon resonance instruments and all needed equipment for sample preparation.

Major scientific results

- The concept of dynamic protein domains is developed. Dynamic protein domains are units of protein structure which retain distinct pattern of large-scale collective motions in the course of protein functioning (S.O. Yesylevskyy, V.M. Kharkyanen).
- The kinetics of recombination of the photomobilized electron in the bacterial photosynthetic center is studied. The number of relaxation components, which are described by the fractional-power-law and could be caused by forming of “taxonomical” states in the system with separated charges is revealed (V.M. Kharkyanen).
- The general theory of the single-file diffusion of multiple strongly interacting particles in a one-dimensional pore is developed, which allows computing any macroscopic characteristic of multi-particle diffusion in the pore and is ready for practical computations and application to the pores of ionic channels and artificial nanopores (V.M. Kharkyanen, S.O. Yesylevskyy).
- The polarizable water model for the coarse-grained MARTINI force field is developed (S.O. Yesylevskyy).
- Development of Pteros molecular modeling library (http://sourceforge.net/projects/pteros/). Pteros is user-friendly and high-performance library for molecular modeling and analysis of molecular dynamics trajectories for C++ and Python programming languages (S.O. Yesylevskyy).
- The methodology of MD simulations of asymmetric and highly curved biological membranes is developed and applied to the large-scale coarse-grained simulation of cholesterol containing

membranes. The methods of determining shape and curvature of the membranes with arbitrarily topology are developed (S.O. Yesylevskyy).

- The methodology of separation of single carbon nanotubes from the bundles, their characterization and creation of the hybrid nanotube-biomolecules systems is created (G.I. Dovbeshko, O.P. Gnatyuk).
- The experimental techniques of enhanced spectroscopy of the biomolecules and their complexes on the metal nanostructured surfaces are developed (G.I. Dovbeshko).
- The model of interaction of the anti-tumor drugs with nucleic acids is developed (G.I. Dovbeshko).
- The SEIRA (Surface Enhanced Infrared Absorption) technique was applied to study the nucleic acids from the tumor cells, conformational properties of the biological molecules adsorbed at the carbon nanotubes and metal nanostructures. Conformational changes in the DNA caused by its interaction with carbon nanotubes are revealed (G.I. Dovbeshko).
- Optical properties of photonic crystals infiltrated by biological molecules and living cells is studied (V.V. Boiko).

Scientific Program

Thursday, October 1

08:30	10.00	Registration	
10:00	10:15	Opening by academician Zagorodnii A.G.	
10:15	10:30	Foreword dedicated to the memory of Prof. Valery Karkyanen by academician Loktev V.M.	
10:30	10:35	Foreword by the director of the Institute of Physics academician Yatsenko L.P.	
Session 1: *Theory and computer simulations*			
Chairmen: ***Yatsenko L.P, Bulavin L.A.***			
10:35	11:05	Chalyi A.V. Dimensional Crossover in Nanoscale Systems	Plenary
11:05	11:35	Eremko A.A. Spin sensitive electron transmission through monolayers of DNA molecules	Plenary
11:35	12:05	Volkov S.N. DNA in the nanoworld	Plenary
12:05	14:15	**Lunch**	
Chairmen: Karachevtsev V.A, Chalyi A.V.			
14:15	14:45	Estrela - Llopis V.R. Glyconanoparticles of noble metals for cancer therapy direct use	Plenary
14:45	15:05	Ermakov V. Effect of low-intensity pulsed electric field on the biogenic synthesis of nanosilver in a cell matrix of living microorganisms	Oral
15:05	15:25	Yesylevskyy S.O. How to get selectivity from unspecific binding? Insight from the modeling of STAT3 inhibitors.	Oral
15:25	15:45	Gogotsy O. Nanodiamonds for drug delivery and other biomedical application.	Oral
15:45	16:05	Perepelytsya S.M. Dynamics and ordering of DNA counterions	Oral
		Coffee - break	
16:00	16:45	Round table: **Perspectives of theory and computer simulations of nanosystems with biological molecules**	
Chairmen: Yesylevskyy S.O			
16:45	18:00	**Poster session**	
Chairmen: Kapustina M.			
		Sakhno T.V. Spectral properties of bis (benzimidazole) perylene dye in organic solvents and polysiloxane matrix containing gold nanoparticles	Poster
		Sychkova S.T. Physical and mechanical properties of radiation modification composites based on PTEE with the addition of nanofiller	Poster
		Semenov A.A. A germicidal ultraviolet disinfection of drinking water	Poster
		Kosevich M.V. Modeling of functioning of Methylene Blue dye in	Poster

		nanotechnology-related systems under mass spectrometric conditions	
		Andreev E.O. Polyedral sorption modelling of nucleotides on gold SERS and SEIRA substrates	Poster
		Morozovsky A. N. Mobile defect dynamics and polarization reversal in ultra-thin ferroelectric semiconductor films with mixed ionic and electronic conductivity	Poster
		Hushcha T.O. Internal protein dynamics in human serum albumin and its complexes with ligands	Poster
		Boiko. V.V. Vibration spectra of DNA in confined volume of photonic crystal	Poster
		Kovalova D.O. The electronic spectra of copper nanoparticles - ceftriaxone conjugate	Poster
		Kuzmenko M.O. The investigation of interaction between oxyresveratrol and fullerenes in the aqua solutions	Poster
		Panas I. Magnetic and fluorescent bifunctional nanocomposites for biomedical application	Poster
		Pidhirnyi D.V. Coherent anti-Stokes Raman scattering (CARS) and imaging of DNA molecules	Poster
		Pokrovskiy V.O. The laser desorption mass spectrometry in biomedical studies	Poster
		Berezetska N. M. Fractal dynamics and statistical parameters of interferentional electromiogramma, in diagnostics of Parkinson disease	Poster
		Feniuk O. Carbon nanotubes and graphene in catalysis	Poster
		Nikolaienko T.Yu. On the He-He bond paradigm in C60-nanoconfinement	Poster
		Onanko A.P. Mechanical properties of nanocomposites based multiwall carbon nanotubes and automated system of anisotropy analysis	Poster
		Morozovsky N.V. Ferroelectric-like melanin features: humidity effect on current-voltage characteristics and transient currents	Poster
		Schur O.L. Catalytic Activity of Metal Complexes Immobilized at “Fullerene-Silica” nanocomposite	Poster
		Rakytska T.L. Schiff bases complexes immobilized at nanosilica as catalysts in ozone decomposition	Poster
		Cherniavskyi Y. Interaction of the fullerenes with asymmetric lipid membranes	Poster

Friday, October 2

Session 2: *Physical aspects of biomolecular nanosystems*			
Chairmen: Shestopalova A. V, Pokrovskiy V.O.			
10.00	10:30	Kapustina M. Super-resolution fluorescence microscopy for imaging	Plenary

		of biological systems	
10:30	11:00	Solyanik G. I. Cell and cancer: from theory to therapy	Plenary
11:00	11:30	Karachevtsev V.A. Hybridization of homopolynucleotides on the carbon 9anomater surface	Plenary
11:30	11:50	Lisetski L.N. DPPC multilamellar structures with membranotropic agents of different chemical nature: SAXS and differential scanning calorimetry studies	Oral
11:50	12:10	Mitsa V. Energy dependent luminescence of realgar, auripigment and As2S3 glass with anticancer nanophase realgar inclusion	Oral
12:10	12:30	Vidybida A.K. Cooperative mechanism for improving discriminating ability in natural sensory systems and its utilization in artificial nano - chemo sensors	Oral
12.30	12.50	Gorelik V.S. Raman scattering on lattice and internal vibrations in polycrystalline biological amino acids	Oral
12.50	13.10	Machnii T.I. Raman microscopy of human cultured skin fibroblasts	Oral
12.10	12.30	Catalano F. Factors ruling the adsorption of proteins on silica nanoparticles, spectroscopic investigation of the interface events and their influence on cell uptake	Oral
12.30	12.50	Terenetskaya I.P. Provitamin D photochemistry in ordered medium: from fundamentals to applications	Oral
12:50	14.20	**Lunch**	
Session 3: *Enhancement of the optical processes in biomolecules by nanostructured metal surfaces.*			
Chairmen: Chegel V.I.			
14:20	14:50	Chegel V. I. Factor of dielectric substrate in chip-based plasmon enhanced fluorescence spectroscopy	Plenary
14:50	15:10	Pavlik B.D. Enhancement of nonlinear phenomenons in biomolecules due to near – field effects in metal nano structures	Oral
15:10	15:30	Dovbeshko G.I. Could graphene be used as substrate for biomolecules in Surface Enhanced Spectroscopy	Oral
15:30	15:50	Kosminska Yu. Synthesis of metallic micro and nanostructures with developed surface for biosensing applications	Oral
15:50	16:10	Molebnyi V.V. New methods in measurement of human eye parameters	Oral
16:10	16:30	Dragan A.I. Metal Enhanced Fluorescence: recent progress and perspectives	Oral
16:30	17:00	**Coffe-Break**	
17:00	17:30	Round table: **Mechanisms and application of surface enhanced effects**	
Chairmen: Dovbeshko G.I.			
17:30	18:00	Round table**: Super high resolution in optics**	

Chairmen: Kapustina M.			
18:00	19:00	**Poster session**	
Chairmen: Karachevtsev V.A			
		Drapikovskyi M.A. Investigation of the kinetics of photoinduced electronic transitions in nanostructures of bacterial reaction centers	Poster
		Horbenko Yu.Yu. Polymer-magnetic nanocapsules for biomedical application	Poster
		Kalinkevich O.V. Modeling biomineralization on nanoscale : the influence of lipids and blood components on calcification in vitro	Poster
		Krasnikova A.O. Phospholipid membrane medium as a matrix to study drug-lipids interactions	Poster
		Kuperman M.V. Iron (II) clathrochelates in complex with albumin: determination of binding site and pH-studies	Poster
		Losytskyy M.Yu. Energy transfer in polystyrene-vinylpyridine-chlorin e6 nanosystem for photodynamic therapy	Poster
		Pashynska V.A. Mechanistic electrospray mass spectrometry study of nanoclusters of cardioprotector flokalin and amino acids	Poster
		Poluian N.A. The effect of irradiated solvent on properties of antitumor antibiotic doxorubicin	Poster
		Serdenko T.V. Analysis of chlorophyll fluorescence in wheat leaves by exponential deconvolution	Poster
		Kovalska V.B. Metal-enhanced fluorescence of trimethine cyanine dyes bound to amyloid fibrils	Poster
		Bokotey O. Studies of nonlinear optical properties for Hg3X2Y2 (X = S, Se, Te; Y= Cl, Br, I) gyrotropic crystals	Poster
		Gnatyuk O.P. Raman scattering of oligonucleotides	Poster
		Danilov M.O. Synthesis, properties and application of graphene materials derived from multi - walled carbon nanotubes.	Poster
		Sementsov Yu.I. Three – dimensional structure from graphene nanoplates	Poster
		Kozik O. Implementation of high dispersed carbon and oxide materials	Poster
		Galagan N.P. Properties of nanosized silica and silica based biocomposites in cryomedia containing thawed bovine sperm	Poster
		Obrazkov O.G. Temperature programmed desorption (TPD) mass spectrometry in surface chemistry studies of	Poster

		nanostructured systems	
		Zobnina V.G. Simulation of protonated nitrogen bases interactions with carbon nanotubes	Poster
		Kukharenko O. Determination of refractive index of GaAs crystal using time-domain terahertz spectroscopy	Poster
		Lopatynska O.G. Plasmonic properties of gold trigonal and hexagonal nanoprisms deposited on the glass substrates	Poster
		Chernii S. Effect of the macrocyclic metal complexes on lysozyme amyloid aggregation	Poster
		Gnatyuk O.P. FTIR spectroscopy study of BN nanoparticles interaction with cancer cells	Poster
		Danilenko I. Zirconia biomaterials for medicine	Poster
		Svyda Y.Y. Peculiarities of Cytosine Molecules Luminescence under Different Excitation Conditions	Poster
		Krasnenkov D.S. Study of buccal cells telomere length in the Ukrainian population	Poster

Saturday, October 3

Session 4: *Interactions of biomolecules with the nanoparticles and nanostructured surfaces.*			
Chairmen: Pokrovsky V.O.			
10:00	10:30	Demchenko A. Novel prospective 11anomaterials for fluorescence sensing and Imaging	Plenary
10:30	11:00	Dzyadevych S.V. Conductometric enzyme biosensors	Plenary
11:00	11:30	Gorban O. Nanosized zicrconia/oligomeric shell: influence of zirconia surface	Plenary
11:30	12:00	Gayvoronsky V.Ya. Harmonic Nanoparticles – Biolabeling Based on Nonlinear Optical Approach	Plenary
12:00	12:30	Yashchuk V. Electronic exitations energy transfer in biopolymers	Plenary
12:30	12:50	Ilchenko O.O. Quantitative analysis of chemical compounds from three-dimensional Raman maps: biological samples application	Oral
12:50	14:15	**Lunch**	
Session 5: *Hybrides of the biomolecules with carbon nanostrucrures*			
Chairmen: Demchenko A.P., Karachevtsev V.A.			
14:15	14:35	Kurnosov N.V. Influence Of Amino Acid Doping On Photoluminescence Intensity From Semiconducting Carbon Nanotubes	Oral
14:35	14:55	Zarudnev E.S. Noncovalent interaction of heterocyclic organic molecules with graphene: DFT study	Oral
14:55	15:15	Dovbeshko G. I. Microcrystalls of DNA constitutes on the graphene surface: second harmonic generation	Oral

15:15	15:35	Dekaliuk M. Carbon nanoparticles as fluorescent probes for apoptosis detection	Oral
15:35	15:55	Cherpak V. Efficient white OLED based on the orange and blue exciplex emission	Oral
15:55	16:15	Grynko D.A. The approach for fabrication of single nanocrystal devices	Oral
16:15	16:25	**Coffe-Break**	
16:25	17:00	Round table: **New material for cellular and molecular sensing**	
Chairmen: Soldatkin O.L.			
17:00	17:40	Round table: **Applications of graphene-based materials**	
Chairmen: Karachevtsev V.A			

Sunday, October 4

		Excursions and depature of participants

Disclaimer

The abstracts are published as provided by the authors. The organizing committee is not responsible for any mistakes, typos or formatting errors in the abstracts.

Session I

Physics of the nanosystems based on biological macromolecules. Theory and computer simulations.

Dimensional Crossover in Nanoscale Systems

A. V. Chalyi

Bogomolets National Medical University, Kyiv, Ukraine

Two types of dimensional crossover (DC) are studied. The 1st type (DC-1) corresponds to transition from 3*D* bulk to 3*D* finite-size systems. In this case the dependence of physical properties on thermodynamic variables (temperature, density, pressure, etc.) in bulk systems with linear sizes $L >> \xi$ may convert into dependence of these properties on linear sizes in finite-size systems with $L < \xi$. The 2nd type (DC-2) corresponds to the case when a further decreasing of linear sizes in confined systems may be treated under certain conditions as the change of spatial dimensionality *D* (for example, $3D \Leftrightarrow 2D$ crossover in slit-like pores or $3D \Leftrightarrow 1D$ crossover in cylindrical pores). Smooth transition of the effective critical exponent ν of the correlation length ξ from $\nu = 0.625$ for D=3 to $\nu = 1$ for D=2 as well as comparison of theoretical results and experimental data are examined for systems in reduced geometry.

Spin sensitive electron transmission through monolayers of DNA molecules

A. A. Eremko

Department of Physics of Biological Systems, Institute of Physics, Natl. Acad. of Sci. of Ukraine. Prospect Nauki, 46, Kiev-03039, Ukraine.

E-mail: eremko@bitp.kiev.ua

The transmission coefficient for electrons passing through the helically shaped potential barrier which is produced by DNA molecules is calculated. It is shown that the spin-orbit interaction (SOI) acting on the moving electron in the helical potential breaks the spin degeneracy in the momentum space. As the result the spin polarization of a transmitting electron depends on the spin polarization of an incident electron, the strength of the SOI, and the width of a monolayer (the length of DNA). This is in qualitative agreement with experimental observation and for reasonable SOI coupling parameters can provide a rather good quantitative agreement with the experimental data.

DNA in the nanoworld

S.N. Volkov

Bogolyubov Institute for Theoretical Physics. NAS of Ukraine

The structural transformations of DNA double helix at the nanoscale determine the unique properties of macromolecules needed to implement the mechanisms of biological processes in living cells. The development of micromanipulation technique of individual molecules at the nanoscale, new results on X-ray analysis of DNA double helix fragments and experiments on macromolecules compaction greatly expanded the understanding of the structural features of DNA.

It became clear the need of macromolecules mechanics study at small relative small to its size scales. It was found that the formation of localized deformation patterns of DNA at the nanoscale serves as markers for specific mechanism for genetic activity regulation of the macromolecule. In experiments on DNA micromanipulation it is found unexpected threshold effects of macromolecule overstretching and unzipping under action of external force of pN level. The need to create a new mechanics of DNA became apparent as a result of the rapid development of nanotechnology, where the DNA double helix is used as a constructional element.

The report shows the possibility of describing the double helix structural changes at the nanoscale in the frame of approach developed by author. The approach describes the processes of DNA macromolecule deformation taking into account their coupling with the conformation of the double helix. The approach allows predicting the possible transformation of DNA macromolecules under action of different external factors in biological processes and under applying of the double helix as a part of design of DNA-based nanomaterials. It is shown that the unique features of DNA macromolecules at the nanoscale is conditioned by fundamental property of the double helix – it conformational polymorphism.

Dynamic self-organization on biomolecular and cells levels and some relations to nanotechnology

Alexander O. Goushcha

Advanced Photonix Inc., Camarillo, California & Institute of Physics, NASU, Kyiv

This presentation summarizes some of the most interesting, recently reported phenomena related to dynamic self-organization in biomolecular systems and tissues. The processes and interactions controlling self-organized behaviors are discussed for protein folding, bioenergetics, charge transfer, and other processes. Determination of feedback mechanisms, control parameters, and order parameters needed to completely define the self-organized behavior and dynamics of a particular system is discussed.

We analyze also recent advances in nanotechnology of metal oxides, which dynamics show surprising similarity to biomolecule systems. Nonlinear dynamics of metal oxides allows designing new imaging systems having several orders of magnitude lower energy consumption and thousands time faster than the best currently available systems based on CMOS technology.

Influence of conformational rearrangements of sugar-phosphate backbone on the electrostatic potential of DNA minor grooves in aspect of protein-DNA recognition

M.Y. Zhytnikova, A.V. Shestopalova

Usikov Institute for Radiophysics and Electronis, Natl. Acad. of Sci. of Ukraine, Acad. Proskura str., 12, Kharkiv-61085, Ukraine.
E-mail: shestop@ire.kharkov.ua, a_shestopalova@mail.ru

Electrostatic interactions play a crucial role in many fundamental biochemical processes on the nanoscale level. In particular, the electrostatic properties of nucleic acids are important for protein-DNA interactions and recognition. DNA is highly charged and polymorphic molecule and proteins use these properties for indirect or shape readout of the target DNA sequences [1]. It was shown [2], that the structural distinction of sugar-phosphate DNA backbone from its canonical B-form characterized by unusual shape, width and polarity of the DNA grooves facilitate reliable recognition of the target DNA sites by proteins.

In this study we calculate electrostatic potential of free B-DNA fragments available in structural data bases (PDB, NDB) in order to determine possible influence of conformational transitions in sugar-phosphate DNA backbone on electronegative potential of the minor groove.

Results of our calculations and their analysis demonstrated that switching from canonical backbone to alternative conformations influences on the size and electronegativity of minor groove. Analysis of sequence-specificity allows make conclusion that electronegativity of AT base pairs is considerably higher than of GC pairs. It should be noted that switching of deoxyribose to A-liked form for some GC pairs from set of investigated fragments leads to increasing of electronegativity of minor groove. We also obtained that short fragments of unbound DNA with identical sequences may have different distribution of electrostatic potential in minor groove and, in contrary, distribution of minor groove electrostatic potential for different sequences can be similar.

Thus changing of size and electrostatic potential of minor groove as a result of sugar-phosphate backbone rearrangement and their sequence-specificity may be a signal for detecting proteins their specific DNA sequences.

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Effect of low-intensity pulsed electric field on the biogenic synthesis of nanosilver in a cell matrix of living microorganisms

V.N. Ermakov[1], **V.I. Podolska**[2], **O.Yu.Voitenko**[2], **Z.R. Ulberg**[2]

[1]*Bogolyubov Institute for Theoretical Physics, Natl. Acad. of Sci. of Ukraine, 14B Metrologichna St., Kyiv 03143, Ukraine. e-mail : vlerm@bitp.kiev.ua*
[2] *Ovcharenko Institute for Biocolloidal Chemistry, Natl. Acad. of Sci. of Ukraine, 42 Vernadsky blvd., Kyiv 03142, Ukraine. e-mail : IBCC@ukrpost.ua*

The peculiarities of biogenic synthesis of silver nanoparticles in cell matrix of *Candida albicans*, *Pseudomonas fluorescens* and *Lactobacillus plantarum* cultures were investigated.

The new respiration-depended hypothesis on nanoparticle biosynthesis by microorganisms was proposed. This hypothesis is based on discovered respiratory activity (RA) of bacteria after low-intensity treatment by pulsed electric field (IEF) [1]. The hypothesis assumes that in microorganisms with increased resistance to silver the poisonous ions can reach the cytoplasm membrane and be reduced by the electrons which take part in the redox reactions of the respiration centers. The nanoparticles can be produced in periplasm space of bacterial cells according to electrochemical reaction $nAg^+ + ne^- \rightarrow nAg$. The proposed approach makes it possible to control the RA of bacteria. Thus this method is a tool to control the nanosilver production. Respiration-depended hypothesis and experimental results are in good agreement.

The features of biogenic nanosilver synthesis by microorganisms having the thick cell wall (*C.albicans*, *L. plantarum*) were studied. It was observed that in this situation the main role is played by existence of agents capable of reducing silver ions according to reaction: $RCHO+2Ag^+ +3OH^- \rightarrow RCOO^- +2Ag^0+2H_2O$ and availability of ordered structures similar to artificial *S*-layers [2]. The treatment of lactic acid bacteria biomass with IEF under Ag^+-ion sorption procedure as well as the *S*-layers disintegration with guanidinhydrochloride reagent promotes the red shift of SPR band or splitting of spectra maximum depending on IEF frequency. Such parameters can be associated with formation of discrete size nanoparticles or with formation of large clusters including very small particles.

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How to obtain selectivity from the unspecific binding: comparative computational study of STAT3 inhibitors

S.O. Yesylevskyy [1], C. Ramseyer [2], C. Borg [3]

[1] *Department of Physics of Biological Systems, Institute of Physics, Natl. Acad. of Sci. of Ukraine. Prospect Nauki, 46, Kiev-03039, Ukraine.*
E-mail: yesint4@gmail.com

[2] *Laboratoire Chrono-Environnement,University of Franche-Comté, Besançon, France.*

[3] *Inserm 1098, EFS Bourgogne Franche Comté, University of Franche-Comté, Besançon, France.*

Human signal transducer and activator of transcription 3 protein (STAT3) is known to be involved in cancer development by promoting cancer cell growth. Suppression of STAT3 activation inhibits growth of the cancer cell. In contrast, homologous and structurally similar STAT1 protein is thought to play an opposite role in the cancerogenesis. That is why any prospective anti-cancer drugs, which inhibit STAT3, should not suppress the activity of STAT1. The most promising way of inhibiting STAT3 protein to date is suppressing dimerization by targeting its SH2 domain. However, close sequence and structure similarity of the SH2 domains of STAT1 and STAT3 make selective inhibition of STAT3 a challenging task.

In this work we compared the binding of several non-peptidic inhibitors of STAT3 to STAT1 and STAT3 proteins by comprehensive ensemble docking simulations. Two well-known selective STAT3 inhibitors sta-21 and bp-1-102 were used as well as the family of five inhibitors recently designed by the authors [1]. The flexibility and dynamics of STAT1 and STAT3 monomers in water environment are accounted by the all-atom molecular dynamics simulations.

It is shown that the binding of all studied inhibitors is unspecific, while the selectivity to STAT3 is caused by "selectivity by distraction" mechanism. The inhibitors bind strongly to DNA-binding domain of STAT1 which distracts them from the SH2 domain of STAT1. In STAT3 there is no such distraction and effective concentration of inhibitors on the SH2 domain is higher which leads to stronger inhibitory effect.

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Dynamics and ordering of DNA counterions

S.M. Perepelytsya, S.N. Volkov

Bogolyubov Institute for Theoretical Physics, NAS of Ukraine

DNA macromolecule is a polyelectrolyte shaped as the double helix with the negatively charged sugar-phosphate backbone outside and nucleic bases inside. Under the natural conditions the charge of DNA is neutralized by positively charged metal ions (mostly Na^+ or K^+), stabilizing the structure of the double helix. Due to homogeneity of the double helix backbone the structure of DNA with counterions tethered to the phosphate groups may be considered as ordered system resembling to the lattice of ionic type (ion-phosphate lattice). The study of dynamics and ordering of counterions around the double helix is of paramount importance for the understanding mechanisms of DNA biological functioning.

Using developed dynamical model of DNA ion-phosphate lattice [1-5] the frequencies and Raman intensities of the vibrational modes for right-handed *B*-and *A*-forms, and left-handed *Z*-form of the double helix with Na^+, K^+, Rb^+, Cs^+, and Mg^{2+} counterions were calculated. In the case of alkali metals the frequencies of ion-phosphate vibrations decrease from 180 to 100 cm^{-1} and the Raman intensities increase as the counterion mass increases. In the case of *Z*-DNA the mode of ion-phosphate vibrations (near 150 cm^{-1}) is related with the motions of Mg^{2+} counterions in the minor grove of the double helix. Our results give the interpretation of the experimental Raman spectra for different DNA forms.

To study the structurization of counterions around the double helix the molecular dynamics simulations have been performed for the DNA fragment d(CGCGAATTCGCG) in water solution with the alkali metal ions Na^+, K^+, and Cs^+ [6]. The computer simulations were performed within the framework of NAMD software package. The results have showed that the Na^+ counterions interact with the phosphate groups directly from outside of the double helix and via water molecules at the top edge of DNA minor groove. K^+ ions are localized mostly in the grooves of the double helix, and the Cs^+ ions penetrate deeply inside the minor groove being bonded directly to the atoms of nucleic bases. The cesium ions counterions form a structured system of charges in the DNA minor groove that can be considered as ionic lattice.

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Nanodiamonds for drug delivery and other biomedical applications

H. Gogotsi[1], **Y. Gogotsi[2]**, **V. Mochalin[2]**, **I. Uvarova[1]**, **O. Gogotsi[3]**, **Y. Zozulya[3]**, **B. Malinovskiy[3]**, **V. Zahorodna[3]**

[1]Frantsevich Institute for Problems of Materials Science of NASU, 3 Akademika Krzhyzhanovs'koho St, Kyiv 03680, Ukraine
E-mail: hgogotsi@gmail.com
[2]A. J. Drexel Nanomaterials Institute, and Department of Materials Science and Engineering, Drexel University, Philadelphia, PA 19104, USA
E-mail: gogotsi@drexel.edu
[3]Materials Research Centre, 3 Akademika Krzhyzhanovs'koho St, Kyiv 03680, Ukraine
E-mail: agogotsi@mrc.org.ua

Abstract

Carbon nanomaterials hold tremendous potential in addressing the two major issues faced by our society: providing energy and improving healthcare. Nanodiamond powder produced by detonation synthesis is one of the most promising carbon nanomaterials for drug delivery and theranostics [1], [2]. Diamond particles have a ~4-5 nm stable core and a large surface area with tailorable surface chemistry. Nanodiamonds have unique optical, mechanical and thermal properties. These properties have recently started to attract much interest for different biomedical applications [3]. Rich surface chemistry, nontoxicity and good biocompatibility of diamond nanoparticles make them attractive in biomaterial applications [4].

The development of new methods for obtaining free nanodiamond particles opens up new possibility for targeted drug-delivery systems that overcome cell membranes, various biological markers, systems intended for determination of the concentration of bioactive agents in living organisms, and others applications [5]. For tissue engineering scaffolds, the non-toxic fluorescent nanodiamond introduced into biodegradable polymers provides increased strength, visual monitoring, and enhanced biomineralization [6].

Nanodiamond (ND) particles are increasingly being utilized as diagnostic, imaging, and therapeutic agents in biomedicine [7]. In the area of biomedical imaging and diagnostics, luminescent nanodiamond with NV centers, as well as chemically modified fluorescent nanodiamond, hold tremendous potential to replace toxic semiconductor quantum dots, thus bringing this exciting potential application one step closer to the clinics [8]. Before nanodiamonds could be applied, they have to undergo multistage purification, characterization and surface modification. Various approaches of surface modification and functionalization of nanodiamond allow to enhance and control drug adsorption for prolongation of drug action and chemical binding of the drugs for sustained drug release for their further use as a drug delivery platform. As for drug delivery, this study mainly focuses on adsorption of antibiotics that will be discussed in detail. We demonstrate results of physical−chemical study of the adsorption of doxorubicin, polymyxin B and rifampicin on nanodiamonds.

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Interaction of the fullerenes with asymmetric lipid membranes

Y.Cherniavskyi[1], **S. Yesylevskyy**[1]
[1] *Department of Physics of Biological Systems, Institute of Physics, Natl. Acad. of Sci. of Ukraine.*
Prospect Nauki, 46, Kiev - 03039, Ukraine.
E-mail: echerniavskyi@gmail.com

Since the discovery fullerenes have attracted much attention because their unique properties. Numerous potential applications of fullerenes in different fields, including biomedical science, were proposed. Their applications in biomedical science are mostly related to their ability to entrap small molecules [1] and high permeability through biological barriers [2].

In the present study we use coarse-grained molecular dynamics to investigate the process of interaction of fullerenes with curved asymmetric DOPC/DOPS bicelle. To distinguish the effects guided by asymmetricity of lipid composition in the different leaflets of the membrane, we compared our data with the data collected from the simulation of symmetric DOPC bicelle. We analyzed dynamics of clusterization and evolution of the fullerene aggregates inside the bicelle. Comparison of the mean and Gaussian curvature of DOPC/DOPS bicelle with and without fullerenes shows that fullerenes do not significantly influence both mean and Gaussian curvatures of the membrane, but increase ordering of the lipid tails, which are in direct contact with the fullerenes. Also we studied the influence of the mean and Gaussian curvatures on the distribution of fullerenes inside the bicelle. Our data suggest that the effects of membrane curvature should be taken into account in the studies concerning permeability of the membranes to fullerenes and fullerene-based drug delivery systems.

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Modeling of functioning of Methylene Blue dye in nanotechnology-related systems under mass spectrometric conditions

M.V. Kosevich, V.S. Shelkovsky, O.A. Boryak, V.G. Zobnina, V.V. Orlov,
V.A. Karachevtsev

[1] *Department of Molecular Biophysics, B. Verkin Institute for Low Temperature Physics and*
Engineering of the National Academy of Sciences of Ukraine,
Lenin Avenue, 47, Kharkov-61103, Ukraine
E-mail: mvkosevich@ilt.kharkov.ua

Redox - active cationic dye Methylene Blue (MB), used for more than a century as a pharmaceutical, currently is finding novel applications caused by developments in bionanotechnology. Functioning of MB in nanodevices is based on redox properties of MB that is its ability to shuttle electrons between the components of a device. Redox activity of MB depends on the monomer-dimer ratio in a system. Changes of the redox and aggregate state of MB on variation of external conditions can be monitored my means of mass spectrometry [1, 2], that is described in the present communication.

The first example relates to difference in the mechanisms of relaxation of MB excitation by UV irradiation, which is reduction reaction for dimers and generation of singlet oxygen for monomers, essential for photodynamic therapy. Occurrence of reduction of MB dimers and its absence for monomers adsorbed at biomimetic negatively charged layers is demonstrated by desorption mass spectrometry [1].

In the next example similar effect of occurrence or absence of reduction under mass spectrometric conditions permitted us to establish the form of adsorption of MB on nanostructures in nanocomposites [2]. In particular, monomeric form of adsorption of MB cations on carbon nanotubes in a sensor-destined composite, which enhances the hydrophilicity of the composite, was proved.

In the framework of investigating molecular mechanisms of MB affect on peptides related to neurodegenerative diseases, oxidation of cysteine amino acid to cystine in the presence of MB was demonstrated recently in our model experiments.

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Polyhedral model of nucleotides adsorption on the SERS and SEIRA substrates

Ye Andreyev

Department of Physics of Biological Systems, Institute of Physics, Natl. Acad. of Sci. of Ukraine. Prospect Nauki, 46, Kiev - 03039, Ukraine.

Strong adsorptions of biological macromolecules with the gold surfaces are important to maximize the signals of the surface-enhanced IR or Raman spectra. It is known that the energy of interaction of the molecule with the surface is determined by their mutual orientation. In the case of gold substrates for spectroscopic purposes the interaction of the molecules of the surface determines the enhancement of the spectroscopic signal in the individual regions of the spectrum. The question of optimal orientation of the molecules on the surface become important. It is known that enhancement of the optical signal depends on the method of adsorbing the molecules and on the morphology of the surface (roughness or existence of nano-sized crystals) [1].

In this work the method of polyhedral modeling [2,3] is used to select the most probable architectures of the surface layer of biomolecules on gold surface. The polyhedral model [3] is based on three empirical assumptions:

1) The form of the region of space occupied by particular atom can be represented by geometric primitives - convex polyhedra with long edges equal to the Bohr radius, and 4-, 5-, 6-pentagonal faces.

2) The interatomic distances are thus determined by tight packing of such polyhedra.

3) Binding sites are determined by pairing the faces with equal number of vertices, while directions of the bonds are perpendiculars to the centers of the paired faces.

Fig. 1 shows thymine in the polyhedral representation. Fig. 2 shows this molecule adsorbed on gold surface in the alpha phase.

There is a principal difference in the sets of polyhedra which are necessary to describe metal and the biomolecule. There are no square faces in nucleotide and no pentagonal faces in gold. Thus these objects can only be paired by hexagonal faces. However, no hexagonal faces of gold are accessible due to its lattice geometry in the case of flat surface.

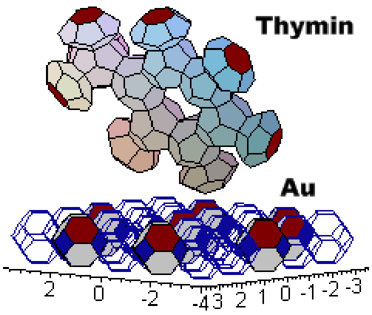	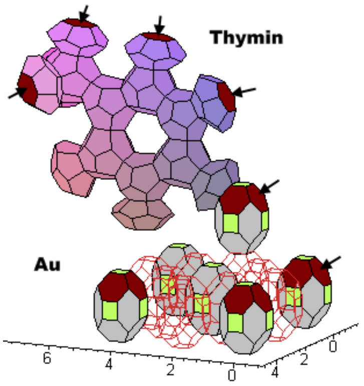
Fig. 1. Thymine near the gold surface in the alpha phase (polyhedral representation)	Fig. 2. Thymine bonding on a single projecting atom.

The binding problem can be solved by forming a specific rough structure on the gold surface, which exposes hexagonal faces to biomolecule. This finding confirms experimental observation about importance of the surface roughness for efficient binding of biomolecules on the gold surfaces in the surface enhanced spectroscopy experiments.

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Internal protein dynamics in human serum albumin and its complexes with ligands

T.O. Hushcha, **I.Ye. Shchechkin**[1], **S.O. Yesylevskyy** [2]

[1] *Department of Cellular Signaling Systems, Institute of Bioorganic Chemistry and Petrochemistry, Natl. Acad. of Sci. of Ukraine. Murmanska Street,1, Kiev-02094, Ukraine.*
E-mail: hushcha @bpci.kiev.ua

[2] *Department of Physics of Biological Systems, Institute of Physics, Natl. Acad. of Sci. of Ukraine. Prospect Nauki, 46, Kiev-03039, Ukraine.*
E-mail: yesint4@gmail.com

Although human serum albumin (HSA) has a well-defined globular equilibrium configuration in the native state, molecular structure and energy fluctuations play an important role in HSA ligand binding activity. In the present paper we examined the temporal regularities of relaxation of molecular structure and energy fluctuations that occur in aqueous solution of uncomplexed HSA in comparison with those for HSA complexed with low molecular ligands. The data have been obtained by combination of experimental and theoretical techniques involving the measurements of sound attenuation spectra and the simulations of molecular dynamics with pressure and temperature jumps.

The series of discrete components related to the processes of local and global conformational changes of protein as well as various phases of mobility of bulk and hydration water molecules have been identified in the relaxation spectra of the studied systems. It has been ascertained that binding of endogenous as well as exogenous ligands with HSA results in drop of all frequencies of conformational transitions determined in the study and in reduction of residence time of water molecules in the protein hydration layer.

Predominance of entropy effect in binding thermodynamics of heterogeneous ligands with human serum albumin have been shown. This effect should be taken in consideration when selecting factors of regulatory influence on the protein, for instance, under drug design. The found regularities of conformational dynamics of HSA and ligand-HSA complexes can be used in development of methods of medicinal chemistry and prediction of pharmacokinetics of drugs. In addition, the obtained data form the basis for decoding molecular spectra of protein solutions obtained by various experimental methods in time interval from 0.5 ps to 0.5 μs.

Modeling biomineralization on nanoscale: the influence of lipids and blood components on calcification *in vitro*

O.V. Kalinkevich, **A.N. Kalinkevich, S.N. Danilchenko**

Department of Radiation Biophysics, Institute of Applied Physics, Natl. Acad. of Sci. of Ukraine.
Petropavlovskaya St., 58, Sumy-40000, Ukraine.
E-mail: bio20001@yandex.ru

Modeling of mineralization *in vitro* helps to understand its mechanisms in different pathologies and develop effective means of its prevention. Such simulation studies significantly complement the modeling of clinical picture using animals, as they allow to investigate the pathogenesis at the molecular level [1].

We investigated the effect of blood plasma on the precipitation of calcium phosphates in physiological solution containing calcium and phosphate ions. X-ray diffraction data show that in these conditions both in the control and in the experimental solutions the less stable phase of brushite is formed. Addition of blood plasma significantly affects the processes of brushite crystallites forming in the investigated model system. Probably, blood plasma contains components that promote self-organization of crystals in different way than under normal synthesis. The results indicate different crystallographic and morphological properties of nanocrystalline brushite depending on the availability of blood plasma that was used as an additional component in the synthesis. The introduction of blood plasma substantially alters the texture of the samples.

To create a model of an atherosclerotic plaque, the films based on chitosan with the addition of cholesterol were synthesized. The use of chitosan for modeling a vascular wall in our experiments allowed excluding influence of collagen on the mineralization process. According to X-ray diffraction analysis, on the films with cholesterol the hydroxyapatite phase was formed during the incubation. This correlates with the results of the bulk synthesis of calcium phosphates in the presence of cholesterol and other lipids of blood vessel medium (phospholipids). In case of cholesterol, nanocrystalline hydroxyapatite is the only crystalline phase in the formed calcium phosphates, while adding phospholipids leads to the predominant formation of brushite.

Calcification in the presence of cholesterol and phospholipids also gives morphologically different structures (on micro- and nanolevels) and probably occurs by different mechanisms. Thus, cholesterol can contribute significantly to the formation of a stable insoluble mineral phase under physiological conditions in a relatively short period of time.

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Fractal dynamics and statistical parameters of interferentional electromiogramma in diagnostics of the Parkinson disease

N.M. Beresetskaya[1], **I.N. Karaban**[2], **M.A. Chivkikliy**[2], **E.P. Lukhanina**[3]

[1] *Department of Physics of Biological Systems, Institute of Physics, Natl. Acad. of Sci. of Ukraine. Prospect Nauki, 46, Kiev-03039, Ukraine.*
Institute
[2] *Parkinson's disease center, Institute of gerontology Natl. Acad. of Medical Sci. of Ukraine, Kiev-03039, Ukraine.*
[3] *Department of brain physiology, A.A. Bogomoletz institute of physiology Natl. Acad. of Sci. of Ukraine, Kiev-03039, Ukraine.*

One of the most informative parameter for Parkinson disease (PD) are the amplitude and spectral characteristics of electrical miogramme (EMG). Recently new parameter of interferential EMG was proposed as a marker of PD. We made the analysis of fractal dynamics and statistical parameters of interferential EMG for PD patients with comparison of aged donors.

We stated the main features of PD in patients:

1) Herst coefficient could decrease below 0,5 (to 0.1-0.2) that is a characterization negative autocorrelation.

2) Time series of EMG at rest are more complex in PD patients than in healthy individuals.

3) Correlation properties of short and long time series of EMG signals in PD patients are statistically different from the reference group.

The most interesting point is that distorted miogramme activity is observed in 43% of healthy relatives of PD patients. This correlations increases with age.

Thus fractal analysis and statistical data are informative parameters of the state of muscle activity of PD patients and could be used to estimate the stage of PD disease.

MOBILE DEFECT DYNAMICS AND POLARIZATION REVERSAL IN ULTRA-THIN FERROELECTRIC SEMICONDUCTOR FILMS WITH MIXED IONIC AND ELECTRONIC CONDUCTIVITY

Nicholas V. Morozovsky,[1] Olexander V. Varenyk,[1] Svetlana L. Bravina,[1] Sergei V. Kalinin, [3] and Anna N. Morozovska,[1]

[1]*Institute of Physics, NAS of Ukraine, 46, Prospect Nauky, Kyiv 03028, Ukraine*
[2]*The Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37922, USA*

Theoretical study of mobile defect dynamics influence on polarization reversal in ultra-thin ferroelectric semiconductor (FES) films with different contribution of mixed ionic-electronic conductivity was performed. The main theoretical results are confirmed by experimental observation of polarization reversal charge-voltage and current-voltage characteristics.

Self-consistent numerical solution of Poisson’s equation for electric potential and space charge coupled with continuity equations for mobile charge carriers (donors and electrons) and time-dependent Landau-Ginzburg-Devonshire equation for ferroelectric polarization have been obtained and analyzed. The analysis reveals that the Vegard stresses (chemical pressure) leads to the redistribution of both charged and electro-neutral defects in order to decrease the effective stress in FES-lattice. At that, built-in and depolarization electric fields set conditions for accumulation of screening ionic and electronic space charges near the FES-electrode interface.

The shape of charge-voltage and current-voltage hysteresis loops of FES is affected by mobile defect dynamics, which is defined by complex frequency dependent interplay between the donors, electrons and lattice. The complexity originates from the local strain caused by steric effects, inverse flexoelectric effect (the strain linear response to a polarization gradient) and Vegard stresses. Depending on the ratio of donor, electron and phonon characteristic times to applied ac voltage period, charge-voltage loops transform from right tilted to left tilted and current-voltage loops transform from single-hysteretic with clockwise path-tracing to double-hysteretic with counter-clockwise path-tracing.

The first type of loops is characteristic for submicron $Pb(Zr_{0.54}Ti_{0.46})O_3$ FES films with low-mobile O^{2+}-vacancies and the second type of loops is characteristic for subsurface layer (~100 nm thick) of FES ionic proustite, Ag_3AsS_3, with high-mobile Ag^+-cations. Intermediate cases have been observed for meso-porous Si under wet air pulse impact giving start to protonic (H^+) conductivity.

Session 2:

Physical aspects of biomolecular nanosystems

Super - resolution fluorescence microscopy for imaging of biological systems.

Maryna Kapustina,

University of North Carolina at Chapel Hill

For centuries, cell biology has been based on light microscopy and at the same time has been limited by its optical resolution. It has been commonly accepted that a lens-based (far-field) optical microscope cannot resolve structural details smaller than about half the wavelength of light ($\lambda/2$).

Recently, several new technologies, called super-resolution fluorescence microscopy, have been developed that bypass this limit. These technologies are based on the discovery that the diffraction barrier of far-field fluorescence microscopy can be radically overcome using basic molecular transitions. That allows an order of magnitude improvement in spatial resolution in all three dimensions. Among diverse methods of super-resolution fluorescence microscopy that provide subdiffraction spatial resolution are: saturated structured-illumination microscopy (SSIM), stimulated emission depletion microscopy (STED), photoactivated localization microscopy (PALM), and ground state depletion microscopy (GSDIM). Our lab uses the GSDIM method (Leica SR GSD 3D microscope) to investigate the cytoskeleton structure in rounded cells and compare with the cytoskeleton in attached and fully spread cells.

Our preliminary investigations have already revealed important features of the cell rounded state: highly folded surface morphology that allows fast and efficient cell shape transformation, and specific distribution of myosin II which is underlying and supporting this folded membrane-cortex architecture.

Although all super-resolution methods have their own weaknesses and are far from been fully developed, the observation of previously unresolved details demonstrates the great promise of super-resolution fluorescence microscopy in elucidating biological processes at the nano-scale level.

Cell and cancer: from theory to therapy

G.I. Solyanik

Department of Experimental Cancer Therapeutics, R.E. Kavetsky Institute of Experimental Oncology, Pathology and Radiobiology, Natl Acad of Sci of Ukraine, Vasylkovskaya, 45, Kiev 03022, Ukraine, E-mail: gsolyanik@gmail.com

In the frame of modern conceptions, cancer is related to a group of diseases with pathologic division of cells capable for invasion and dissemination into distant organs and tissues of an organism. Such understanding of the problem has been gained just in the middle of XIX century due to the development of physical methods, in particular microscopy what led to the formation of cellular theory of living organism constitution. Spatial-functional structure of an organism is determined by three main cellular functions: differentiation, division and migration. Herein, more than 99% of cells in an adult organism are differentiated (these cells don't divide while their life span is significantly shorter than that of an organism). Approximately 1% is occupied by constantly dividing auto-stem cells which provide the renewal of body's cellular composition. In contrary to normal stem cells, pathologic stem cells are insensitive for inhibition of cell division with the differentiation factors (what leads to their uncontrolled division).

The loss of stem cell sensitivity to the effects of differentiation factors determines an initiation of tumor process. Such understanding of the process of tumorigenesis has formed the basis for the main types of cancer therapy: stimulation of differentiation; inhibition of migration (antimetastatic action); inhibition of cell division (cytostatic action); tumor cell killing (cytotoxic action). In XIX-XX centuries cytotoxic cancer therapy (CCT) aimed on cancer cell elimination at any cost, has achieved the highest development. However, low specificity of anticancer action of CCT and its high toxicity toward normal organs and tissues have motivated the elaboration of new approaches for cancer therapy – development of target anticancer drugs capable to inhibition of tumor growth and dissemination due to their interactions with specific molecules involved in the growth and progression of malignant tumors. Providing of highly specific tumor-associated intermolecular interaction is the place of application of actively developing nanotechnology. Nanoparticles can be used to target biomarkers or antigens that are highly specific to cancer cells. Also, nanotechnologies are capable to provide specific delivery of the target drug to the tumor due to an easy penetration of nanostructures through biologic membranes. However, an effective use of nanotechnologies in oncology has some limitations. For instance, cancer targeting is highly dependent on cancer specific biomarkers. Not just any nanoparticle will work.

Also nanoparticles need to be biocompatible and stable with low side effects and toxicity. Although no clinical trials have been performed yet with nanoparticles the development of nanotechnology can turn cancer into chronic, but manageable disease with low risk of death.

Hybridization of homopolynucleotides on the carbon nanotube surface

V.A. Karachevtsev

B.I. Verkin Institute for Low Temperature Physics and Engineering, Natl. Acad. of Sci. of Ukraine.
47 Lenin ave., Kharkov, 61103, Ukraine.
E-mail: karachevtsev@ilt.kharkov.ua

Genetic information obtained from the analysis of the base sequences in DNA is extremely important in biomedical engineering, molecular biology, genetic testing, clinical diagnostics of genetic diseases, environmental safety and food development. The utilization of novel carbon nanomaterials for the DNA biosensor development opens up new opportunities for ultrasensitive and label-free detection of biomolecular processes. The hybridization of complementary DNA strands on single-wall carbon nanotubes (SWNT) is promising for the development of DNA biosensors.

In this contribution the recent results of DNA/RNA hybridization on SWNT are reviewed. The special attention is payed to optical methods for observation of hybridization of homopolynucleotides. Experimental results indicate that hybridization on the nanotube surface has a slow kinetics, the behavior of which differs essentially from fast hybridization of free polymers. The duplex obtained is characterized with the reduced thermostability and a lower hyperchromic coefficient than it was observed with the duplex formed without the nanotube. These experimental features point to the defectiveness in the structure of the double polymer formed on the nanotube surface.

Computer simulation (employing Molecular Dynamics) showed that the strong interaction of nitrogen bases with the nanotube surface weakens significantly hybridization of two complementary oligomers as the surface prevents the necessary conformational mobility of the polymer to be hybridized. Besides, the strong base-base ordering in a single-stranded polymer free in suspension also impedes fast hybridization with a complementary strand adsorbed to the nanotube. In the review the question is discussed how the efficiency of the hybridization on the carbon nanotube will be changed if π-π stacking interaction between nitrogen bases in the target polymer is decreased or the binding of the bases with the nanotube surface of the probe polymer is weakened.

In the contribution DNA-pairing interactions exploiting for creating multicomponent structures from carbon nanotubes suspended in water are also considered. The recent researches demonstrate that DNA is one of the most promising functional nanomaterials, which can be programmed to self-assemble into sophisticated nanostructures.

DPPC multilamellar structures with membranotropic agents of different chemical nature: SAXS and differential scanning calorimetry studies

L.A.Bulavin[1], D.V.Soloviov[2], A.I.Kuklin[2], L.N.Lisetski[3], N.A.Kasian[3], A.O.Krasnikova[3], O.V.Vashchenko[3], A.V.Zinchenko[4]

[1]Taras Shevchenko National University of Kyiv. 4 Academician Glushkov Ave., Kyiv 03022, Ukraine
[2]Joint Institute for Nuclear Research. 6 Joliot-Curie str., Dubna, Moscow region, 141980, Russian Federation
[3]Institute for Scintillation Materials of STC "Institute for Single Crystals", NAS of Ukraine, 60 Lenin Ave., Kharkov 61001, Ukraine; lisetski@isma.kharkov.ua
[4] Institute for Problems of Cryobiology and Cryomedicine, NAS of Ukraine, 23 Pereyaslovskaya Str., Kharkiv 61015, Ukraine

Multilamellar structures formed in DPPC/water/glycerol and DPPC/water/oxyethylated glycerol systems were studied by small-angle X-ray scattering (SAXS) and differential scanning calorimetry (DSC methods). The effects of glycerol, oxyethylated glycerol and other membranotropic agents (MTA) on the lamellar repeat distance D were compared in gel, ripple and high-temperature (L_α) liquid crystal phases of the hydrated phospholipids.

Under substitution of oxyethylated glycerol $OEG_{n=5}$ for water in DPPC vesicles the multilamellar structure is retained in all the $OEG_{n=5}$ concentration range. The lamellar repeat period D is gradually decreasing in all phases, and the mesomorphic phase transition temperatures are increasing with $OEG_{n=5}$ concentration. The ripple phase disappears above ~30%. Unlike similar systems with glycerol, no clear evidence of interdigitated $L_{\beta I}$ phase formation could be noted from SAXS data.

It has been shown that membranotropic agents (MTA) of different chemical classes introduced into DPPC systems can lead to different types of $D(T)$ behavior in L_α phase. The sign of the MTA-induced shift of the repeat distance correlates with the sign of dD/dT at temperatures above the melting transition.

Energy dependent luminescence of realgar, auripigment and As_2S_3 glass with anticancer nanophase realgar inclusion

V. Mitsa[1], I. Fekeshgazi[1], A.Marton[1], R. Holomb[1], M.Veresh[2]

[1]*Research Institute of Solid State Physics and Chemistry, Uzhhorod National University, Uzhhorod, Ukraine*

[2]*Wigner Research Centre for Physics of the Hungarian Academy of Sciences, Budapest, Hungary, E-mail:v.mitsa@gmail.com*

In PL spectra of long term aged on air g-As_2S_3 with realgar nanophase inclusions at $W_{ex.4}$= 3.1 eV dominate the band near 2.8 eV, typical for PL band of $As_2O_3xnH_2O$ solution (Fig.1). In such case in Raman spectra appeared the band at 680 cm^{-1}[1], known for As $(OH)_3$. In PL spectrum exited by $W_{ex.2}$ = 2.48 eV ($\lambda_{ex.2}$ = 500 nm) there are picking distinct PL bands at E_1* = 2.04 and E_2* = 2.26 eV (Fig.1). Last PL maxima are known for oxides phases As_2O_3 and As_2O_5. Formation oxide phases in g-As_2S_3 may be connected with photo-aging. Rally, at $W_{ex.1}$=1.77 eV in PL spectra we observed the PL band at E_1=1.72 eV , typical for realgar (r-As_4S_4). At $W_{ex.2}$=2.25 eV (Fig. 2), at which intensively occur polymorphic transformation realgar to pararealhar [1], the PL maximum with E_1 shifted to E_2 = 1.86 eV (we assigned to p-As_4S_4) and at E_1* = 2.04 (As_2O_3) is seen shoulder. Photo-degradation of surface with increasing energy of excitation to $W_{ex.4}$= 3.1 eV accompany with formation the band near 2.8 eV (Fig.2), less intense than in case long term aged on air surface (Fig.1).Similar, as above mentioned PL bands ,where found in PL spectra crystalline auripigment As_2S_3 and r-As_4S_4. Processes natural and photo-aging should by take into account during medical treatment by realgar.

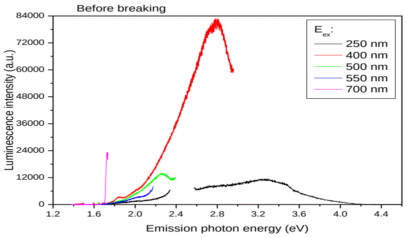

Fig.1. PL spectra aged on air g-As_2S_3

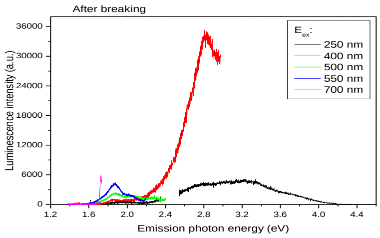

Fig.2. PL spectra freshly fractured g-As_2S_3

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Cooperative mechanism for improving discriminating ability in natural sensory systems and its utilization in artificial nano-chemo-sensors

A.K.Vidybida[1]

[1] Department of Synergetics, Institute for Theoretical Physics, Natl. Acad. of Sci. of Ukraine.
Metrologichna str., 14B, Kyiv-03680, Ukraine.
E-mail: vidybida@bitp.kiev.ua

Natural sensory systems of various modalities, such as olfaction, hearing, vision, have remarkable discriminating ability. The primary reception of an external stimulus happens at the level of individual receptor cells. In olfaction, the primary reception happens at the level of individual receptor molecules an olfactory receptor neuron (ORN) is populated. The discriminating ability of the receptor molecules arises from their different dissociation constants during binding with different odor molecules. In this case, selectivity seems to be quite moderate. At the same time, odor selectivity can be very high at the level of whole organism.

We propose that the selectivity improvement is due to threshold-type reaction to external stimuli, which is characteristic of nervous cells. In the olfaction, the ORN can fire an output spike if a large number of its receptor molecules are bound with odor molecules. This necessitates a kind of cooperativity between the receptor molecules in order to trigger the ORN. Our purpose here is to estimate the selectivity of chemoreceptor neuron as compared with that of its primary receptor proteins, as well as to investigate possible benefits if the above mechanism is implemented in artificial nano-chemo-sensors. In this course we study the stochastic process of binding-releasing of odor molecules at the ORN. This process brings about an adsorption-desorption noise.

The characteristics of this noise, such as mean time of being above / below the firing threshold, can be quite different for different odors. Based on the exact expressions found for the mean times, we conclude that the odor selectivity of ORN can be much higher than that of its individual receptor molecules [1]. The idea is applied to artificial chemical sensor of small size [2].

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Raman scattering on lattice and internal vibrations in polycrystalline biological amino acids.

V.S. Gorelik[1], **G.I.Dovbeshko**[2], **A.S. Krylov**[3] ,
A.M. Negriyko[2], **V.P. Sverbil**[1], **L.I. Zlobina**[1]

[1] P.N. Lebedev Physical Institute of the Russian Academy of Sciences, Leninskij pr. 53, Moscow, 119991, Russia, E-mail:gorelik@sci.lebedev.ru

[2] Department of Physics of Biological Systems, Institute of Physics, Natl. Acad. of Sci. of Ukraine. Prospect Nauki, 46, Kiev-03039, Ukraine.
E-mail: matinelli@gmail.com

[3] L. V. Kirensky Institute of Physics SB RAS, Akademgorodok 50,bld. 38, Krasnoyarsk, 660036, Russia, E-mail: shusy@iph.krasn.ru

Crystals of biological amino acids have low point symmetry and are constructed from chiral molecules: $NH_2-(HC_2R)-COOH$. The results of spontaneous Raman scattering spectra in some crystalline amino acids (D-asparagine, L-lysine, DL-tyrosine, DL-tryptophan) are presented. Raman spectra were recorded at wide frequency region (6-4000 cm^{-1}) with the help of triple monochromatic spectrometer T-64000.

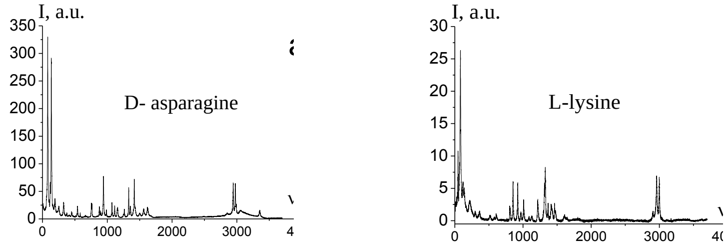

Fig.1. Raman spectra of polycrystalline D-aspagine(a) and L-lysine(b)

We have observed very intense low frequency Raman satellites, corresponding to libration of amino acid molecules. Recently we have recorded intense low-frequency band with maximum at 26 cm^{-1} in dry DNA [1]. The presence of high finesse libration modes in amino acids may lead to resonant interaction of such modes with corresponding DNA modes in biological systems.

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Raman microscopy of human cultured skin fibroblasts

T. I. Makhnii[1], O. O. Ilchenko[1], Yu. V. Pilgun[2], R. A. Slipets[1], A. S. Reynt[1],
O. K. Koliada[1], V. M. Kucharskii[1], D. S. Krasnenkov[1], V. V. Moseiko[1]

[1] D. F. Chebotarev State Institute of Gerontology, NAMS of Ukraine, 67 Vyshhorodska St., Kyiv, Ukraine
[2] Faculty of Radio Physics, Electronics and Computer Systems, Taras Shevchenko National University of Kyiv, 64/13 Volodymyrska St., Kyiv, Ukraine
** E-mail: tanya@geron.us*

One of the problems that can be solved by Raman microscopy is the study of influence of different kind of drugs and chemicals on animal cells. Many types of substances can pass through cellular membrane and accumulate inside the cell. As an example – dimethyl sulfoxide (DMSO) known as cryoprotectant which has ability to rapidly enter into the cell and prevent damage of cells during slow freezing by forming hydrogen bonds with liquid fraction of cytoplasm and reducing salt concentration. It was shown that presence of dimethyl sulfoxide in culture medium can change the cell surface markers and gene expression [1]. Also it has low acute and chronic toxicity for animals [2]. Because of DMSO toxicity, it is advantageous to ensure that DMSO is absent in the cell culture before autotransplantation. Raman spectroscopy can be used to control presence of DMSO in primary human fibroblasts after thawing.

To make it possible Raman spectra of the cell culture should be continuously monitored in time. Spontaneous Raman effect has relatively low efficiency ($I_{Raman} \sim 10^{-7}–10^{-11} \times I_{laser}$) therefore typical pixel dwell time for different samples varies from hundreds of milliseconds to hundreds of seconds in the case of CCD detector. In such conditions total acquisition time per Raman map with dimensions 100x100 pixels can takes hours. In order to decrease the total time of measuring the 2D Raman map of the cell structure we designed high speed line-focus Raman microscope, which decrease acquisition time 400 times. This allows us to make time-lapsed measurements of Raman spectra for a number of fibroblasts simultaneously, and provide enough data for statistical analysis and to reliably control concentration of DMSO in the culture before autotransplantation.

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Quantitative analysis of chemical compounds from three-dimensional Raman maps: biological samples application

O. O. Ilchenko[1], Yu. V. Pilgun[2], R. A. Slipets[1], A.S. Reynt[1],
O.K. Koliada[1], V.M. Kucharskii[1], T. I. Makhnii[1], D. S. Krasnenkov[1]

[1] *D. F. Chebotarev State Institute of Gerontology, NAMS of Ukraine, 67 Vyshhorodska St., Kyiv, Ukraine*
[2] *Faculty of Radio Physics, Electronics and Computer Systems, Taras Shevchenko National University of Kyiv, 64/13 Volodymyrska St., Kyiv, Ukraine, E-mail: aleksey@geron.us*

Raman microscopy can provide quantitative information about distribution of chemical compounds in the object of study. Successful determination of concentration of species in multicomponent mixture from three-dimensional Raman maps via chemometrics methods depends on solving a number of experimental and theoretical issues:

- ensuring system stability during measurement process (time stability of laser power, fluctuations of detector sensitivity, mechanical vibration protection, etc);
- chemomectrics techniques only work well with small number of species (no more than 5-8 components);
- decomposition algorithms may produce erroneous results when spectral peaks are shifted and broadened due to intermolecular interaction between components.

To address these problems line-focus Raman microscope was designed and constructed for high speed quantitative analysis of Raman spectral maps. System stability was verified by measuring spectra of multicomponent liquid mixtures with known concentration profiles and further decomposition analysis. The possibility of application of multivariate curve resolution-alternating least squares (MCR-ALS) [1] in the case of multicomponent mixture was also investigated. It was shown that hybrid technique for decomposition using library spectra and MCR analysis can increase the total number of species for which quantitative information can be successfully obtained. Unknown spectral and concentration profiles can be found correctly if N−1 spectra of components in the mixture remain fixed during MCR-ALS analysis.

Described techniques were applied to three-dimensional Raman maps of mouse skin. Raman spectra of major components in *stratum corneum* were measured in water solutions for further application as known components during decomposition and MCR analysis. There were keratin, ceramides, lactate, water and natural moisture factor (NMF) constituents as arginine, ornithine, citrulline, serine, proline, glycine, histidine, alanine, PCA (pyrrolidone carboxylic acid) and UCA (urocanic acid) [2, 3]. It was shown that the distribution maps of listed and even unknown components can be obtained using proposed hybrid technique which combines decomposition and MCR-ALS analysis.

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Provitamin D photochemistry in ordered medium: from fundamentals to applications

I.P. Terenetskaya

Department of Optical Quantum Electronicvs, Institute of Physics, Natl. Acad. of Sci. of Ukraine. Prospect Nauki, 46, Kiev-03039, Ukraine, E-mail: teren@iop.kiev.ua

Photoisomerization of provitamin D_3 (7-dehydrocholesterol) is the first step of vital process of vitamin D_3 synthesis in human skin under solar UVB (280-315 nm) irradiation. Previtamin D first formed by the photoinduced hexadiene ring-opening, is then converted into vitamin D_3 via [1,7]-sigmatropic hydrogen shift.

In solutions, the photosynthesis of previtamin D is a complex branched network of monomolecular isomerizations with the most efficient reversible *cis-trans* isomerization into tachysterol [1].

Significant increase in previtamin D *cis-trans* photoisomerization efficiency with increasing concentration of initial protamin D was observed in liquid crystals (both nematic and cholesteric) at room temperature. But with heating the effect becomes less noticeable and in isotropic phase it disappears that indicates on the collective character of *cis-trans* isomerization in LCs due to the medium ordering [2].

The principal differences between chiral properties of provitamin D photo-isomers in the H-bonding LC and in the routine nematic LCs were found, and the hypothesis on specific interaction of provitamin D molecule with molecules of the LC matrix has been offered.

These studies resulted in the possibility of visual following the photoreaction course in real time, i.e. developing personal UV biodosimeter for direct assessment of the vitamin-D-synthetic capacity of sunlight and artificial UV sources [3,4].

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Effect of the macrocyclic metal complexes on lysozyme amyloid aggregation

V. Kovalska[1], S. Chernii[1], V. Cherepanov[2], M. Losytskyy[1], I. Tretyakova[3], O. Varzatskyy[3], S. Yarmoluk[1]

[1] Institute of Molecular Biology and Genetics, NASU, 150 Zabolotnogo St., 03143 Kyiv, Ukraine
[2] Institute of Physics, NASU, Nauky Ave 46, 03680 Kyiv, Ukraine
[3] Institute of General and Inorganic Chemistry, NASU, 32/34 Palladin Ave., 03680 Kyiv, Ukraine, *E-mail: chernii.sv@gmail.com*

Formation of the unsoluble protein aggregates - filamentous amyloid fibrils is associated with a number of harmful human disorders, among which there are neurodegenerative diseases, amyloidosises, type II diabetes. This causes a request for the development of agents able to suppress or change the pass of fibrillization reaction. Recently we discovered the high anti-fibrillogenic activity of the macrocyclic metal complexes in the insulin aggregation reaction. Axially-coordinated phthalocyanines are able to inhibit strongly the fibrils formation or redirect this reaction to the generation of small-size oligomeric aggregates. The cage metal complexes – iron (II) clathrochelates reduce the intensity of fibril formation and prevent their lateral "super-aggregation".

Here the studies of the effect of the phthalocyanine with axial styryl fragment (PcHfQStr) and hexa-phenylcarboxy iron (II) clathrochelate (Vz375) on the aggregation of other amyloidogenic protein lysozyme ia reported. The fluorescent assay used to monitor the kinetics of the aggregation reaction has shown the reduction of the intensity of the amyloid-sensitive fluorescent probe in the presence of both metal complexes that is due to the decrease of the amount of the final amyloid aggregates. The deviations of the protein intrinsic fluorescence observed during the aggregation allow suggesting that presence of metal complexes promote the intensity of protein conformation changes (partial denaturation) on the early stages of reaction.

The atomic force microscopy was used to study the effect of the macrocyclic metal complexes on the morphology of lysozyme amyloid aggregates. For the free protein, the formation of short linear amyloid aggregates with diameter of 3 – 7 nm and length of 0.1 – 0.6 μm was observed. The presence of PcQSt and Vz375 redirects the aggregation and both compounds induce the formation of significantly longer filamenteous aggregates mainly with the diameters 1.5 – 3.5 nm and the length up to 2-3 μm (Fig).

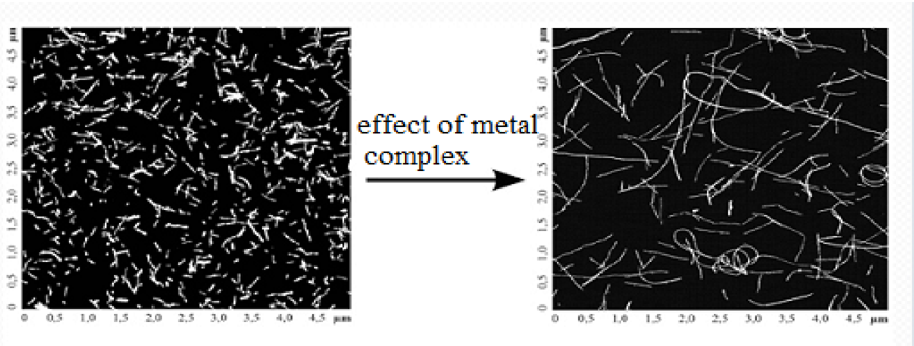

Fig. Lysozyme aggregates formed by free protein (left) and induced by Vz375 presence (right).

We consider that presented results support an interest to the further study of macrocyclic metal complexes as agents able to strong governing on the processes of protein aggregation.

The work was supported by STCU-NASU grant 5972.

Properties of films of bovine serum albumin with sodium halides

**G.M. Glibitskiy[1], D.M. Glibitskiy[1], O.A. Gorobchenko[2],
O.T. Nikolov[2], A.D. Roshal[3], M.A. Semenov[1]**

[1] *A. Ya. Usikov Institute for Radiophysics and Electronics, National Academy of Sciences of Ukraine, 12, Academician Proskura Str, Kharkiv 61085, Ukraine.*
E-mail: glibit@ukr.net

[2] *Department of Molecular and Medical Biophysics, School of Radiophysics, V.N. Karazin Kharkiv National University, 4 Svobody Sq, Kharkiv 61022, Ukraine.*

[3] *Institute for Chemistry, V.N. Karazin Kharkiv National University, 4 Svobody Sq, Kharkiv 61022, Ukraine.*

The method of structural analysis of dried films of biological fluids is used for diagnostics in medicine and biology. It is known that iron and copper ions form complexes with bovine serum albumin (BSA); on the other hand, fluorine and bromine ions interact with BSA through electrostatic forces, hydrogen bonding and hydration shell.

The objective of this paper is to study of the relationship between the changes in the texture of BSA films (the specific density of Z-structures) and the ionic composition of the initial BSA solution containing halides of sodium and iron, as well as their fluorescence characteristics in the UV range.

The changes in the specific density of Z-structures were analyzed for the cases of concentration decrease of chlorine ions (when replaced by fluorine or bromine ions) and concentration increase of iron ions to 0.3 mM in BSA solutions. It is shown that the rate of reduction of the specific density of Z-structures is more than an order of magnitude (50 times) greater for films with iron ions than for films with fluorine and bromine ions. It is concluded that the conformational and structural state of protein in the films has changed in comparison to its conformational state in the solution.

Thus, the differences between the means of interaction of fluorine, bromine and iron ions with BSA correlate with the differences in the formation of film textures from solutions BSA with these ions.

Polymer-magnetic nanocapsules for biomedical application

Yu.Yu. Horbenko, **O.I. Aksimentyeva**

Chemical Department of Ivan Franko National University of Lviv, 6/8mKyryla&Mefodia Str. Lviv, 79005, Ukraine.
E-mail: y_bilka@ukr.net; aksimen@ukr.net

In development of novel technologies in biology and medicine of particular interest is the use of functionalized polymer capsules as drug carriers, microreactors, and sensors. Labeling of nanocapsules by luminescent substances (colloidal synthesis quantum dots) provides a possibility to trace their pathways within a tissue, whereas loading them with magnetic nanoparticles allows for manipulation by an external magnetic field gradient. In the present work firstly we obtained the hybrid composites with three functions – magnetic, luminescent and conductive, by modification of the polystyrene-magnetite nanocapsules by luminescent $BaZrO_3$ nanocrystals and by conducting shell of the polyaniline [1]. Obtaining hybrid composites were characterized by SEM, FTIR, XRD, EDAX analysis and cathodoluminescence (CL). It was found that adsorption of $BaZrO_3$ nanocrystals on polystyrene (PS) shell of nanoparticles leads to modification of CL spectra of $BaZrO_3$ with appearance of new bands at E = 1.9, 2.15, 2.45, 3.0 and 3.96 eV; a conducting polymer did not affects the shape of CL spectrum. By XRD analysis it is found that modification of luminescence spectra of composites is caused by changing in substructure of nanocrystals under influence of PS matrix: decreasing of lattice parameter for nano-$BaZrO_3$ in composite; chemical interaction between PS and $BaZrO_3$ confirmed by FTIR spectra [2]. So, the described modifications of CL spectra can be connected with structural changes of $BaZrO_3$ nanograins under influence of the PS matrix.

Conductive polymer shell provides a possibility to control the behavior of nanoparticles by an electric field, and track their movements in biological environments. Obtained results suggest that main contribution in conductivity of hybrid composites has a matrix of polyaniline shell. Introduction of the $BaZrO_3$ nanoparticles would cause an increase in the activation energy of conductivity due to a morphological change in the regions of along-the-chains conductivity.

Proposed method of surface modification may be used for developing biosensors and diagnostic methods in medicine.

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Phospholipid membrane medium as a matrix to study drug-lipids interactions

A.O. Krasnikova[1*], O.V. Vashchenko[1], N.A. Kasian[1], L.N. Lisetski[1], L.V. Budyanskaya[2], Y.M. Al-Muhkhrabi[2], O.V. Maschchenko[2]

[1] *Institute for Scintillation Materials of STC "Institute for Single Crystals", NAS of Ukraine, 60 Lenin Ave., Kharkov 61001, Ukraine; alina_k@isma.kharkov.ua*
[2] *V.N. Karazin Kharkov National University, 4 Svobody Sqr., Kharkov 61022, Ukraine*

Nowadays, great efforts are made to optimize the effects of drugs in therapy. Among the most important factors are processes of drug penetration through the lipid part of cell membrane. Such processes have great influence on intracellular drug concentration and the time scale of drug action. The aim of the present work was clarification of drug-lipids interactions using model lipid membranes.

A number of drugs have been examined by means of differential scanning calorimetry (DSC). These drugs were used as agents affecting the phase states of hydrated 1:1 *L*-α-dipalmitoylphosphatidylcholine (DPPC membrane). Neat active pharmaceutical ingredients (API) were probed in the DPPC membrane, namely amixin, aspirin, azithromycin, fenspirid, metronidazol, miramistin, noobut (fenibut), tranquilar (mebikar), as well as corresponding commercial drugs based on them (see below).

For all API examined, except tranquilar, fluidizing effect on DPPC membrane was established, confirming the possibility of their spontaneous penetration through lipid membrane. Non-monotonous concentration dependences of DSC parameters were observed for azithromycin, which reflect complex mechanism of drug-lipids interactions. Triple splitting of DSC peaks was registered in the presence of noobut, interpreted as noobut-induced lateral segregation in the lipid phase.

Pronounced difference was established between effects of a commercial drug and the corresponding API. For commercial drugs, which contain both API and excipients, the original membranotropic API effects appeared to be smoothed ("Amixin IC", "Aspirin Complex") or amplified ("Azithromycin", "Erespal", "Metrogil", "Noobut IC"). Such effects demonstrate essential importance of exipients for drug-lipids interaction.

For antibiotic azithromycin, a set of its pharmaceutical analogues has been studied in the aspect of their influence on DPPC membrane. It was noted that DSC effects of these analogues were substantially different. The effects observed could be interpreted as interference of membranotropic action of the antibiotic and the corresponding excipients.

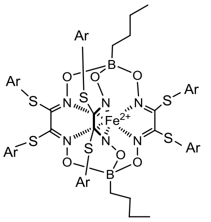
It can be concluded that DPPC membrane is a rather convenient matrix for studies of drug-lipids interactions. Such problems as effects of API concentration, contribution of excipients and comparative influence of pharmaceutical analogues could be elucidated using model lipid systems.

Iron (II) clathrochelates in complex with albumin: determination of binding site and pH-studies.

V.B.Kovalska[1], M.V.Kuperman[1], M.Yu.Losytskyy[1], E. Gumienna-Kontecka[2], O.A.Varzatskii[3]

[1]Institute of Molecular Biology and Genetics, NASU, 150 Zabolotnogo St., 03143 Kyiv, Ukraine, mvkuperman@gmail.com
[2]Chemical Faculty, Wroclaw University, 14 F. Joliot-Curie Str., Wroclaw, Poland
[3]Institute of General and Inorganic Chemistry, 32/34 Palladin Av., Kyiv, Ukraine

The macrocyclic cage complexes iron (II) clathrochelates are reported as compounds able to bind with proteins and this way affect their activity. Besides, these intrinsically achiral complexes could induce the specific signal in circular dichroism (CD) spectra upon such interaction. Hence, there is an interest in the study of guest-host complexes formed by clathrochelates and protein molecules.



Structure of clathrochelates.

In present work, the complexes of hexa substituted carboxyphenyl clathrohelates with bovine serum albumin (BSA) are characterized. For this the specificity of clathrochelates to albumin main binding sites and pH-dependence of the protein-ligand interaction were studied by fluorescent and CD spectroscopy.

The clathrochelate binding site was determined by the competitive displacement with site specific albumin binders warfarin (Site I) and ibuprofen (Site II). According to fluorescent data, clathrochelate is replaced from its complex with BSA only by the excess of warfarin. CD data confirm the displacement by warfarin, but also show the effect of ibuprofen on this complex. Thus, we suggest about preference binding of the clathrochelate to BSA Site I (warfarin site).

The protein fluorescence quenching studies at different pH values (3.7; 6; 7.9) showed that at acidic pH clathrochelates do quench BSA emission less (up to 3 times) in comparison with neutral or basic pH (about 18 times). This could be due to partial protein denaturation or clathrochelates carboxy-groups deprotonation. Besides CD spectra of each clathrochelate-BSA complex at pH values from 4 to 9 have isodichroic points at about 397 and 500 nm. Thus, change of pH causes the transition between two conformations of protein-ligand complex.

Thus, we suppose that pH decrease causes partial destruction of protein binding site; thus, protein-ligand interactions become weaker and conformational changes of BSA-clathrochelate complexes occur. Displacement studies revealed the major involvement of albumin Site I in clathrochelate binding.

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Energy transfer in polystyrene-vinylpyridine-chlorin e_6 nanosystem for photodynamic therapy

M.Yu. Losytskyy[1], L.O. Vretik[1], O.A. Nikolaeva[1], D.A. Getya[1], A.I. Marinin[2], and V.M. Yashchuk[1]

[1] *Taras Shevchenko National University of Kyiv, Volodymyrs'ka Str., 60, Kyiv-01033, Ukraine. E-mail: mlosytskyy@gmail.com*

[2] *National University of Food Technologies, Volodimirska Str. 60, Kyiv, Ukraine*

Photodynamic therapy of cancer is based on the photoexcitation of the photosensitizer molecule introduced into the tumour tissue; this excitation leads to the generation of singlet oxygen that is toxic for the cancer cells. But the main drawback of this method is that the depth of the light penetration into the tissue does not exceed several mm. Thus creating of the X-ray excited sensitizers would possibly solve the problem. Earlier X-ray stimulated luminescence of the hematoporphyrin sensitizer was demonstrated for the nanoparticles (NP) containing polystyrene (PS), vinylpyridine (VP), 2,5-diphenyloxazole (PPO) and hematoporphyrin [1]. The energy transfer was supposed to occur from PS to PPO and further to hematoporphyrin, but this process was not studied and not proved. Here, in the frames of designing the more complex and efficient nanosystems for X-ray excited sensitizing of singlet oxygen, nanoparticles of PS-VP co-polymer with encapsulated PPO were synthesized and excitation energy transfer process from this system to chlorine e_6 photosensitizer was studied.

A microemulsion polymerization was employed for incorporation of PPO into PS-VP nanoparticles (NP) [1]. Latex beads containing organic compound were synthesized directly by the polymerization of a mixture of styrene and VP with initial molar ratio 20 to 1and PPO with potassium persulfate (KPS) as initiator in a micellar aqueous solution of sodium dodecylsulfate (SDS). The diameter of SDS-coated PS-VP-PPO NP was determined by dynamic light scattering technique (intensity distribution) as 8±2 nm. To the solution of the obtained NP the widely used photosensitizer chlorin e_6 was added.

The study of the fluorescence spectra of PS-VP-PPO NP revealed the process of electronic excitation energy transfer from the styrole residues to the encapsulated PPO molecules. Addition of chlorin e_6 resulted in binding of the chlorin molecule with PS-VP-PPO NP, possibly by incorporation into the NP's SDS shell. Electronic excitation transfer from both PPO residues and styrene ones (obviously *via* PPO) to the chlorin molecule was shown.

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Mechanistic electrospray mass spectrometry study of nanoclusters of cardioprotector flokalin and amino acids

V.A. Pashynska[1], M.V. Kosevich[1], A. Gomory[2], K. Vekey[2]

[1] Department of Molecular Biophysics, B. Verkin Institute for Low Temperature Physics and Engineering of the National Academy of Sciences of Ukraine,
47, Lenin Avenue, 61103, Kharkov, Ukraine, E-mail: vlada@vl.kharkov.ua

[2] Institute of Organic Chemistry of Research Centre for Natural Sciences of the Hungarian Academy of Sciences, Magyar tudosok korutja, 2, Budapest, H-1117, Hungary

Recently developed Ukrainian cardioprotective preparation flokalin, fluorine containing derivative of pinacidil – known activator of ATP sensitive potassium membrane channels, have shown the high effectiveness in treatment of myocardial infarction and ischemia in *in vivo* experiments with animals [1]. Meanwhile molecular mechanisms of flokalin interactions with K^+-channels components are not well studied. The current model nanobiophysical study by electrospray ionization mass spectrometry (ESI MS) is devoted to examining the biologically significant interactions of flokalin (Fl) with amino acids (AA) pertained to K^+-channels proteins.

At the first stage of the study solution of Fl in MeOH was investigated by ESI MS for the first time and characteristic mass spectra of the preparation were obtained. The peaks of cationized molecules of FL were recorded: $[Fl:H]^+$, m/z 311, RA 22%; $[Fl:Na]^+$, m/z 333, RA 100%; $[Fl:K]^+$, m/z 349, RA 9 %; $[2Fl:H]^+$, m/z 621, RA 28%; $[2Fl:Na]^+$, m/z 643, RA 68%; $[2Fl:K]^+$, m/z 659, RA 8 %. These peaks can be used as reference peaks to reveal Fl in any biological samples by MS method. At the next stage of the study intermolecular interactions of Fl with selected polar basic and polar uncharged AA, Arg, Lys, Thr, Tyr, Gly and Val, were examined by ESI MS. The spectra of the systems Fl+AA (1:1 molar ratio) contain the ions characteristic of the individual components of the mixtures. However the most interesting result from the nanobiophysical point of view relates to the observation in the spectra the ions of nanoclusters of flokalin with AA molecules. Such ions were quite intensive for Fl+Arg and Fl+Lys systems, less intensive in the spectra of Fl+Thr and Fl+Tyr systems, and absent in the mixtures of Fl+Gly and Fl+Val.

Formation of the stable noncovalent nanobiocomplexes of flokalin with Arg and Lyz was revealed by ESI MS probing that could point to the preferable interaction of flokalin with the K^+-channel domains enriched with these amino acids.

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The effect of irradiated solvent on properties of antitumor antibiotic doxorubicin

N.A. Poluian[1], M.A. Zabolotnyi[1], G.I. Dovbeshko[2], M.P. Kulish[1], O.P.Dmytrenko[1,] R.K. Sagetdinov[3].

[1] *National Taras Shevchenko university of Kyiv, faculty of physics, Glushkova avenue 4g, Kyiv, Ukraine*
E-mail: poluyannadia@gmail.com
[2]*Department of Physics of Biological Systems, Institute of Physics, Natl. Acad. of Sci. of Ukraine. Prospect Nauki, 46, Kiev-03039, Ukraine.*
E-mail: hrysantemka@ukr.net
[3] *KP "Farmaziya" , Pshenychna str. 16, Kiev-03680, Ukraine.*
E-mail: rustem@bigmir.net

Doxorubicin hydrochloride - anthracycline antibiotic, which has high antitumor activity at low selectivity of action,what is suggesting the need for modification of the drug to reduce its toxicity and/or increase its efficiency.

The aim of this work is to study the molecular mechanism of environment's influence on conformational state, oscillating and optical properties of doxorubicin molecules to create new ways of its modifications with increased therapeutic effect and minimize the negative consequences of its use, reducing the dose of the therapeutic load without the formation of toxic products.

In this work was measured IR and UV-Vis spectra of pure drug solutions and samples of compounds Dox with non-irradiated and irradiated solution for infusion, what is predictably provides the formation of stable gas cavities of nanometer size.

The theoretical part of the work includes calculation of IR spectra of doxorubicin in the software package Gaussian using method DFT B3LYP in 6-31G basis.

Radiation exposure of the solvent has significant effect on IR and UV-Vis spectra of molecules of doxorubicin, dissolved in it.

The calculations of vibrational frequencies of doxorubicin in vacuum and in water indicate the change in conformational state of the molecule with taking into account the dielectric constant of the solvent.

Analysis of chlorophyll fluorescence in wheat leaves by exponential deconvolution

T.V. Serdenko[1], **S.M. Kochubey**[2], **Yu.M. Barabash**[1]

[1] *Department of Physics of Biological Systems, Institute of Physics, Natl. Acad. of Sci. of Ukraine. Prospect Nauki, 46, Kiev-03039, Ukraine.*
E-mail: tais.serdenko@gmail.com

[2] *Institute of Plant Physiology and Genetics, Natl. Acad. of Sci. of Ukraine. Vasylkivska Street, 31/17, Kiev-03022, Ukraine.*

The shape of induction curve of chlorophyll fluorescence in leaves of plants is caused by the several processes. They are the following - energy exchange in the light-harvesting antenna, photochemical transformation and an electron outflow from reaction centers. The shape of the induction curve becomes simpler when electron transport from the reaction centers is blocked because only energy exchange in antenna gives contribution.

In the present work an analysis of the shape of this curve is executed for leaves of 4 varieties of wheat. The original method is applied for analyzing of a component structure of the induction curves by deconvolution of them on the exponents. The method uses the additional basis which is orthogonal in relation to the initial one. Step-by-step procedure is used for selection of number of exponents, their amplitudes and decrements to obtain the best approximation of the experimental curve by the sum of these exponents. The procedure is begun with approximation by a single exponent. Then the second one is added and their parameters are varying to reach the maximal optimization. An addition of components and the mutual adjusting of their parameters are repeated till obtaining the best approximation of the experimental curve. Thus, the novel information has been obtained in difference from earlier researches which gave only amplitude values.

Revealing of only three components in the analyzed induction curves is in a good accordance with finding out only three types of pigment-protein complexes in thylakoid membranes of chloroplasts. Thus, an analysis of induction curve of chlorophyll fluorescence can be used as an effective instrument for investigation of the state of photosynthetic membranes.

Investigation of the kinetics of photoinduced electronic transitions in nanostructures of bacterial reaction centers

Yu. M. Barabash[1], M. A. Zabolotnyi[2], M. A. Drapikovskyi[2], M.P. Kulish[2], R. K. Sagetdinov[3]

[1] Department of Physics of Biological Systems, Institute of Physics, Natl. Acad. of Sci. of Ukraine. Prospect Nauki, 46, Kiev-03039, Ukraine.
E-mail: ybar@ukr.net

[2] National Taras Shevchenko University of Kyiv, 46, Kiev-03039, Ukraine. 64 Volodymyrska st., 01033 Kyiv, Ukraine;
E-mail: drapikovskyi.maksym@gmail.com

[3] KP "Farmaziya", Kiev, Ukraine.
E-mail: rustem@bigmir.net

It is known that the absorption of a quantum of light in the reaction centers (RCs) of purple bacteria *Rb. sphaeroides* R-26 causes the photooxidation of the primary donor of an electron, a bacteriochlorophyll dimer (P). Thereafter the excited electron appears at the primary ($\mathbf{Q_A}$) quinone acceptor, passes through a number of intermediate carriers, and then gets into the terminal quinone acceptor ($\mathbf{Q_B}$) [1--3]. The process of localization of an electron at quinone acceptors is defined by the state of intraprotein hydrogen bonds (which are formed, in particular, with participation of water molecules of a solution) and the protonation of the nearest amino acid residues by ionogenic groups and is accompanied by a conformational rearrangement of the molecular complex of RC [2--5]. The information about regularities defining the character of light-activated structural transitions of biomolecules is of independent interest. The conformation determined the bioactivity of a molecule, and the control over structural transitions opens a possibility to use them in molecular electronics.

Despite the great number of publications devoted to the study of photoinduced processes running in RCs, there are the great number of obscurities in their theoretical comprehension. Far from being completed is the development of a model allowing the adequate description of the intramolecular dynamics of an electron under the action of exciting light. The complications arising in this case are caused by both the great number of stages of the process of electron transfer inside the complex of RC and the variety of the transition channels for an electron inside RC. In the simple case, it is considered that RC can be represented in the form of a protein matrix containing some built-in molecules (redox-cofactors) which manifest the donor–acceptor properties relative to the light-excited electron. The electron leaves the donor, a bacteriochlorophyll dimer, appears at the primary quinone $\mathbf{Q_A}$, passes a distance of 30–40 Å through a number of inremediate states, and is stabilized at the secondary quinone-acceptor $\mathbf{Q_B}$, by generating, in this case, the difference of potentials on a photosynthetic membrane. The displacement of the electron induced by exciting light can be described [5] in the frame of of the three-level model with the level of acceptor $\mathbf{Q_B}$ which slowly varies in the process of electron transfer. A change of the energy level of $\mathbf{Q_B}$ is defined by structural transitions in RC and polarization processes in its environment. A change of the energy characteristics of RC must lead to a change of the rate constants of photoinduced electron transitions. At the present time, the kinetics of these most important characteristics of RC is studied slightly.

The posed problem [2, 5] concerning the electron transport in RC is complicated, and therefore the additional simplifying assumptions are used in its analysis [2, 5]. Two of such assumptions are the quasiequilibrium behavior of the ratio of the electron populations on quinones

Q_A and **Q_B** and the independence of this ratio on the intensity of exciting light. The conditions for these assumptions to be valid require the additional analysis.

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Raman scattering of oligonucleotides

G. Dovbeshko[1], O.P. Gnatyuk [1], D. Pidhirnyi[1], O. Feniuk[1], O. Ilchenko[2], D. Krasnenkov[2],

A. Damin[3]

[1]Institute of Physics, National Academy of Sciences of Ukraine, 46 Nauki Ave, Kyiv 03680, Ukraine
[2] D. F. Chebotarev State Institute of Gerontology, NAMS of Ukraine, 67 Vyshhorodska St., Kyiv, Ukraine
[3]Department of Chemistry, university of Torino, Italy

Raman scattering is sensitive tool for DNA molecules study. Here we apply it for oligonucleotide study using different lasers, 785 nm, 514 nm, 422 nm. We used Renishaw inVia microscope in Italy and home-made Raman microscope in Kiev. High levels of sensitivity and stability of the home-made system has been achieved through the use of stabilized diode laser Starbright 785XM with wavelength of 785nm, flat field spectrograph PI IsoPlane320 and highly sensitive and stabilized CCD PI Pylon 400BR Excelon cooled with liquid nitrogen. Similarity of nucleotide spectra obtained under 785 nm excitation with 2 different spectrometers proved a possibility to use home- made spectrometer for conventional measurement.

Under registration of the RS spectra of two oligonucleotides AAAACGCCAGTAAGTGACAGAGTCACCAAATGCTGCACAGAATCCTTGGTGAACAGGC GACCATGCTTTTCAGCTCTGGAAGTCGATGAAACATACG and $(TTAGGG)_{14}$ (Syntol, Russia), synthesized for polymerase chine reaction and purified by polyacrylamide-gel electrophoresis, we got 2 lines in the region of 900-1015 cm-1 (excitation 785 nm) which we could not explain. That is why we decide to check it using other excitation - green and blue lasers). We got the same spectra as those using 785 nm.

We applied gold rough substrate in all our experiments for enhancement the signals from oligonucleotides. After analysis we understood that we have deals with not-purified oligonucleotides. Additional bands come from some compounds used for oligonucleotides synthesis and purification. So it could expect, that primers purity enough for polymerase chine reaction not enough for Raman scattering.

According to our data an additional analysis we concluded that the spectra of nucleotides (97 and 84 bases) are similar the spectra of DNA in the 400-3400 cm-1. So, arising of additional bands could be markers of admixtures. Using a gold substrate, we could register DNA of 1-2 mg/ml concentration in contrast to neutral substrate in conventional spectroscopy (40 mg/ml DNA concentration or more).

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Physical and mechanical properties of radiation modifications composites based on PTFE with the addition of nanofiller

S.T. Sychkova[1], T. V. Sakhno[1], N. V. Sadovskaya[2], S. A. Khatipov[2], Y. E. Sakhno[3]

[1]*University of Economics and Trade, Poltava, Ukraine 36014*
E-mail: sychkova@ukr.net
[2]*Karpov Institute of Physical Chemistry, Vorontsovo Pole street 10,, Moscow, Russia 105064*
[3]*Poltava Institute of Economics and Law of Open International University of Ukraine, Poltava, Ukraine 36000*
E-mail: sakhno2001@mail.ru.

A study of physical and mechanical properties of radiation modification composites based on polytetrafluoroethylene (PTFE) with micro- and nanofillers has been carried out. It was found that an addition of carbon nanotubes (CNT) dramatically changes the morphology of PTFE nanocomposites [1]. Morphology of initial samples was prose containing polycrysralline fibrillar lamellae and loose packing of structural elements. Adhesion of fillers to the matrix found to be weak with poorly resolved interface layer. The values of friction coefficients for nanocomposites with a different CNT content have been determined and their variations within a broad range (more than 70%) have been reported. It was shown that the intensity of linear wear diminishes for all PTFE-based nanocomposites with increasing CNT concentration in the range from 1% to 5% in 6 to 65 times from an initial value, respectively. It was established that modification of such composite caused by g-irradiation lead to significant changes in morphology and reduce linear wear correspondingly. Not irradiated samples originally exhibit a certain level of porosity, the presence of polycrystalline fibrilarlamels and low adhesion of filling material with matrix. Irradiation of CNT/PTFE composite at temperature above the melting point result in formation of spherolites, significant decrease in porosity and improved adhesion of filling material with matrix. Intensity of the linear wear down diminishes for all of composites of PTFE/CNT: with content 1,0; 2,5 and 5,0 % CNT in ~ $4\cdot10^3$; $2,5\cdot10^3$ and $3,5\cdot10^2$ times from an initial value, accordingly.

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Properties of nanosized silica and silica based biocomposites in cryomedia containing thawed bovine sperm

N.P. Galagan, E.M. Roytman, V.V. Roy, N.M. Moshkivska , V.O. Pokrovskiy

O.O. Chuiko Institute of Surface Chemistry, Natl. Acad. of Sci. of Ukraine. 17 Gen. Naumov Str., Kyiv 03164, Ukraine

E-mail: nataliyagalagan@gmail.com

Physico-chemical properties of nanosized silica (NS) surface allow synthesis of biocomposites (BC) which may be efficiently used for optimization of biotechnological processes [1]. But the details of such BC effect on cell systems were not studied in detail till now. The aim of present study was the investigation of effect of NS (SiO_2 A-300 produced in Kalush, Ukraine) and its BC with sucrose (SiO_2/Sucr), synthesized in laboratory conditions, on parameters of motion of bovine reproductive cells and on the level of oxygen expenditure.

The experiment was performed with bovine thawed sperm granules, frozen in LGY cryomedium which were delivered to the laboratory from breeding farm (city Brovary, Kyiv region). The biomaterial was mixed with NS and BC in concentrations ($1\cdot10^{-3}$ -$6\cdot10^{-1}$ %). Estimation of gametes vitality was done by four parameters of their movement (namely: number of mobile cells, %; frequency of flagellum rotation, Hz; average velocity, mcm/sec; motion energy, arbitrary units, measured by means of laser Doppler spectroscopy). Program-analytical complex “Spectrolas, Ukraine“ was adopted for estimation of the nanoparticles effect on moving cells and its efficiency was proved experimentally. The dependence of movement parameters upon concentration of nanoparticles in cryomedia was studied. It was found out that BC (SiO_2/Sucr) was most efficient in comparison both with NC and control samples.

The level of O_2 absorption by gametes at concentrations $C_{NC} =1\cdot10^{-3}$% and $C_{BC} =1\cdot10^{-2}$ %, correspondingly, was measured in cuvette with sensor of program-analytical complex in air. In the case of NC it was observed that the less its concentration was, the higher was the level of absorption of O_2 by the cells. At concentration $1\cdot10^{-2}$ % NC the consumption of oxygen by cells was higher by 20,6% with respect to control, while at concentration $1\cdot10^{-3}$ % NC it was higher by 51,7%. After addition of BC to sperm before cryoconservation, the sharp decrease of O_2 absorption was observed, continuing also after their defreezing. It is supposed that modification of NS surface by certain energetic substrates can promote regulation of energy transformations in cells.

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Spectral properties of bis(benzimidazole)perylene dye in organic solvents and polysiloxane matrix containing gold nanoparticles

T.V. Sakhno[1], N.N. Barashkov[2], I.S. Irgibayeva[3], Yu.E.Sakhno[4], Anuar Aldongarov[3],

Artur Mantel[3]

[1]*University of Economics and Trade, Poltava, Ukraine 36014*
E-mail: sakhno2001@mail.ru.
[2]*Micro-Tracers, Inc, 1370 Van Dyke Ave, San Francisco, California, 94124, United State , 4156841506, United States nbarashk@hotmail.com*
[3]*Eurasian National University, 5 Munautpasov st., Astana, Astana Region, Kazakhstan*
[4]*Poltava Institute of Economics and Law of Open International University of Ukraine,* Poltava, Ukraine 36000

Solid polysiloxane (PSi) solutions of Au nanoparticles and mixture of sin/anti-isomers of bis(benzimidazole)perylene dye obtained by reaction of tetrachloroperynone with 4-tret-octylphenol and potassium carbonate in N-methylpyrrolidone solution were prepared by mixing chloroauric acid and dye dissolved in dichloromethane with the vinyl-terminated Psi precursor, following by addition of Si-H containing precursor and in-oven curing for 24 hrs. During the curing procedure, reduction of Au(III) to the zero-valent Au takes place. Absorbance and fluorescence properties of prepared Au/dye/PSi compositions were studied and compared with the spectra of dye in organic solvents and its solid solutions in PSi without Au nanoparticles addition. It was found that introduction of Au nanoparticles of certain concentrations into PSi matrices may lead to significant increase of absorbance of the bis(benzimidazole)perylene dye and in several cases to noticeable increasing in the fluorescence intensity.

A germicidal ultraviolet disinfection of drinking water

A.A. Semenov[1], T.V. Sakhno[1]

[1]Poltava University Economy and Trade, Poltava 36014, Ukraine
E-mail: a-semenov@li.ru

The method of ultraviolet disinfection of water is one of the physical, reagentless methods [1]. These methods have a number of significant advantages over chemical reagent method [2], most of which is the lack of changes in the composition and organoleptic properties (smell, taste). Ultraviolet radiation allows destroy viruses and fungi which do not apply the traditional chemical methods, including chlorination.

Bactericidal effect of ultraviolet radiation acts on the wavelength range of 205-315 nm which leads to photochemical damage of DNA.

The purpose of the proposed technical solution is to simplify the design and reduce maintenance costs while maintaining the efficiency of disinfection of water.

In the known structures devices of productivity and the size of the Rays camera calculated by standard methods [3] using the experimentally determined volumetric dose to inactivate various types of microorganisms H_V. The disadvantage of this approach is that the volume dose H_V depends on the geometry of the camera for exposure and degree of mixing water during irradiation in laminar flow. The layers of water that are closer to the UV lamp - the radiator will get "excessive" dose, and the layers of water are near the chamber walls - not receive required dose (if there is a sufficient the average value H_V). To obtain the required dose of disinfection H_S , the size of the camera for radiation (diameter and length) should provide the required minimum radiation $E_{\min}$. Other areas will receive "excessive" exposure that only increases the reliability of disinfection.

The principle of operation of the device for germicidal disinfection of drinking water based on the following - $E_{\min}$ is calculated from the condition: $H_S \geq 100\frac{m \cdot J}{cm^2}$. Based on the proposed technical solution the series of installations for bactericidal disinfection of drinking water have been developed and successfully used by a number of companies in Ukraine.

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Ferroelectric-like melanin features: Humidity effect on current-voltage characteristics and transient currents

S. L. Bravina, P. M. Lutsyk, A. B.Verbitsky, N. V. Morozovsky
Institute of Physics of NAS of Ukraine, 46 Prospect Nauki, 03028 Kiev, Ukraine

Melanin belongs to the class of poly-functional natural pigmentary macromolecules integrated in 1 - 2 nm sized nanoaggregates and is recongnized as one of promising bio-electronic materials.

Depending on surrounding humidity level melanin always possesses noticeable degree of hydration that strongly influences its physical properties.

The influence of air rarefaction on quasistatic current-voltage (I-V-) dependences and the impact of wet air pulse on dynamic bipolar I-V-loops and transient currents (I-t-curves) and also on unipolar I-V-curves of natural melanin based ITO/melanin layer/ITO on glass planar structures (MPS) have been studied for the first time.

The threshold hysteresis voltage of I-V dependences of MPS under 10^5 Pa and under 50 Pa air atmosphere (≈ 1.5 V and ≈ 0.8 V respectively) are near to the standard electrode potentials of anode water decomposition (E_0 = +1,5 V for polarized and E_0 = +0.815 V for unpolarized electrode).

The pulse of wet air of 95 % of relative humidity and (1-5) s of duration gives rise to sharp increase of the conductance and capacitance of MPS and causes the appearance of the next features: “hump”-like on I-V-loops , “knee”-like on I-V-curves and “step”-like on I-t-curves.

General shape and the main peculiarities of I-V-characteristics of MPS were modelled by series-parallel RC-circuit including two Zener diodes connected in anti-series as nonlinear elements.

The treatment of I-V-loop allowing for I-V-curve shape gives evidence for displacement current maxima similar to ones characteristic for metal-insulator-semiconductor structures under ionic space charge transfer and for ferroelectric materials under polarization reversal.

As a reason of appearance of temporal polar media with reversible ionic space charge transfer and/or ferroelectric-like polarization is considered the water assisted dissociation of some ionic groups of melanin monomer units that significantly influences electrophysical parameters, in particular polarization ability of melanin macromolecular media.

Obtained results disclose the possible capabilities of melanin based memory devices and demonstrate the efficiency of dynamic electrophysical characterization for studying the fast humidity changing effect on the electrical performances of functional bio-electronic devices.

Peculiarities of Cytosine Molecules Luminescence under Different Excitation Conditions

Y.Y. Svyda, M.I. Shafranyosh, M.M. Chavarga, M.I. Sukhoviya, I.I. Shafranyosh

Department of Physics, Uzhgorod National University, Voloshyn Str., 54, Uzhgorod-88000, Ukraine
E-mail: ivanshafr@gmail.com

For solving many problems of modern biophysics, there is needed the information about the mechanisms of the radiation’s influence upon the biomolecules, first and foremost, DNA and RNA and their components. Studying of the luminescence peculiarities under different excitation conditions makes it possible to obtain additional information about the molecules’ physical structure.

We made experimental investigations of the phenomenon of cytosine molecules’ luminescence when electrons excite them. The methodical essence of the experiment consists in the obtaining and studying of the optical spectra in the electric discharge inside the tube filled with cytosine molecules’ steam. The experimental equipment consists of the discharge tube with the molecules’ steam under investigation, high-voltage generator for discharge power, and the system of discharge radiation registration. As a result of the experiments, there was found the discharge radiation in the wavelength range from 200 to 500 nm. There was made the comparison of the obtained spectra with the luminescence spectra of cytosine molecules excited by other factors, in particular, by means of the electron-molecular beams crossing under high vacuum conditions, and also in case of photo-excitation. It is found out that there is observed a certain coordination of the spectra under discharge conditions with those obtained in [1]. However, there are found several new molecular bands for the wavelengths of 281, 295, 348, 398 and 452 nm, which are, in our opinion, connected with the radiation of the cytosine molecules’ clusters. Therefore, the suggested methodical approach makes it possible the investigation of the radiation of molecules’ clusters, including the biologically significant ones.

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Study of buccal cells telomere length in the Ukrainian population

D.S.Krasnienkov[1,2], A.K.Koliada[2], A.M.Vaiserman[2], T.I.Makhnii[2]

[1]Kyiv National Taras Shevchenko University, Institute of High Technologies, prosp. Glushkova 4-g, 03022 Kiev, Ukraine
[2]State institution «Institute of Gerontology of Ukraine's NAMS», Vyshgorodska str. 67, 04114 Kyiv, Ukraine.
e-mail: krasnenkovd@gmail.com

Telomeres are terminal parts of chromosomes consists of tandem repeats (TTAGGG) and shelterins (proteins associated with telomeres). Telomeres prevent chromosome ends from recognizing as a double-strand breaks and fusion with each other. Each cell division, damage by free radicals and specific nucleases leads to telomeres shortening. Telomeres length associated with age and age-related diseases (Alzheimer disease, Parkinson disease, cardiovascular pathology, metabolic disorders and cancer). Various populations is peculiar different dynamics of telomere length in different age groups.

We used monochromatic multiplex quantitative Real-time PCR for measurement of relative telomere length in Ukrainian human population. All 180 buccal epithelium samples were randomly selected from healthy individuals of different ages from 18 to 83 years old. The samples were homogeneous in terms of its distribution into age and sex groups. We obtained data that show the dynamics of telomere length age changes in different age groups of Ukrainian population. We observed that telomere length in men is shorter than in women ($p<0.002$). Also was shown correlation for alcohol intake, smoking and weight with telomere length, correlation coefficients were $r = -0.22$, $r = -0.24$ and $r = -0.33$ respectively.

Session 3:

Enhancement of the optical processes in biomolecules by nanostructured metal surfaces.

Metal Enhanced Fluorescence: recent progress and perspectives

A.I. Dragan[1,2]

[1] Institute of High Technologies, Taras Shevchenko National University of Kyiv, 64,
Volodymyrs'ka St., 01601 Kyiv, Ukraine.

[2] *Department of Protein Engineering and Bioinformatics, Institute of Molecular Biology and Genetics NASU, 150, Akademika Zabolotnoho St., 03680, Kyiv, Ukraine*
E-mail: anatoliy.dragan@gmail.com

Over the last decade Metal-Enhanced Fluorescence (MEF) has emerged as the next generation of fluorescence spectroscopy - near-field fluorescence. However, in contrast to our collective knowledge and understanding of classical far-field fluorescence, we know relatively little. MEF is a consequence of the near-field interactions of fluorophores with the surface plasmons generated in plasmon supporting materials, where the optical properties of the metal afford for a wavelength dependence of MEF.

This presentation will review the results of numerous model experiments including but not limited to determination of the role of the individual metal and mixed metal surface deposits in fluorescence enhancement, influence of a chromophore quantum yield on the MEF effect, the dependence of MEF upon the distance between a chromophore and nanoparticle surface, enhancement of chemiluminescence in proximity to the metal surface, the wavelength dependence of the luminescence enhancement. Also, the existing theoretical views on the nature of the MEF will be compared.

Multifarious applications of the MEF effect in biomedical sciences will be considered and discussed.

Factor of dielectric substrate in chip-based plasmon enhanced fluorescence spectroscopy

V. I. Chegel, O.M. Naum, A. M. Lopatynskyi, V. K. Lytvyn

V.E. Lashkaryov Institute of Semiconductor Physics NAS of Ukraine, Kyiv, Ukraine

E-mail: vche111@yahoo.com

In this work we considered for the first time the influence of the dielectric permittivity of the substrate on the local electromagnetic field enhancement near the metal nanostructure, and, as a result, on the emission of organic dye molecules near its surface. To simulate the relevant parameters, dipole approximation method was applied using dyadic Green's function for spherical gold nanoparticles with a radius of 20-80 nm at an external excitation wavelength of 650 nm.

Calculations of volumetric Lippmann-Schwinger equations showed that in the absence of substrate the maximum fluorescence excitation rate enhancement near the surface of the spherical gold nanoparticle with a radius of 20 nm in vacuum is 12.54. In the presence of the dielectric substrate, fluorescence excitation rate always decreases with increasing the value of its dielectric permittivity and equals to 5.59 in the case of glass substrate ($\varepsilon = 2.59$). It was shown experimentally that the fluorescence signal of Rhodamine 6G organic dye can be amplified in 9-38 times near gold nanostructures located on the surface of the glass substrate depending on the separating dielectric layer thickness.

Maximum enhancement was observed with respect to the substrate without nanostructures when the dye molecules were placed at a distance of about 20 nm from metal nanoparticles using the dielectric SiO_2 layer, which is close to the simulation results obtained by means of the developed theoretical approach.

The strong influence of the optical pecularities up discuss system on radiative and non radiative transitions in bio molecules are discussed in details .

B. Pavlik

Aerospace Institute the National Aviation University
Prospect Komarova 1, Kyiv, Ukraine

E-mail: pavlikboris@mail.ru

The model of multilayered spherical and cylindrical cluster and nanoring has developed on the basis of classical Mie theory and maxwell equations in each medium. The specially focus on the problem of tunable radioactive decay of plasmons supported by such a system, and show that the decay time of plasmon in discussed systems can be effectively tuned over two orders of magnitude.

We show theoretically that local field enhancement factors LFEF can reach ultra high values. We also show that the decay rates of void like plasmas are strongly sensitive to the shell-layers thicknesses .

The multyshell modes exhibit ultra shot radioactive life times of the order 1 fs when the thicknesses of shells are much less than the characteristic skins depths. In the opposite case LFEF became more than 100.

Could graphene be used as substrate for biomolecules in Surface Enhanced Spectroscopy

G.I. Dovbeshko

Department of Physics of Biological Systems, Institute of Physics, Natl. Acad. of Sci. of Ukraine. Prospect Nauki, 46, Kiev-03039, Ukraine.

E-mail: gd@iop.kiev.ua

It is known that graphene- based materials could be efficiently used in the optical biosensing. That is why a number of questions arises in connection with it: could graphene be used as a substrate for biological molecules, could be reached giant enhancement in visible and infrared region of spectrum, what is condition for it, what is a mechanism of the enhancement of signals from molecules absorbed on the graphene surface, what molecules could be enhanced, etc.

Experiments on infrared absorption, Raman scattering and coherent anti-Stokes Raman scattering of biological molecules (adenine, thymine, DNA, poly-A) adsorbed on carbon nanostructures: single-wall carbon nanotubes (SWCNTs), multi-walled carbon nanotubes (CNT), graphene nano flakes[2], single and few graphene layers, pyrocarbon (PyC), graphite graphene will be presented and discussed here.

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Synthesis of metallic micro and nanostructures with developed surface for biosensing applications

Yu.O. Kosminska, V.V. Natalych, V.I. Perekrestov

Department of Nanoelectronics, Sumy State University, R.-Korsakova Str., 2, 40007 Sumy, Ukraine, E-mail: y.kosminska@phe.sumdu.edu.ua

As commonly known, developed metallic surfaces are good enhancers of Raman and infrared signals from adsorbed biomolecules and thus are very promising for biomolecules detection applications. Among the technologies of porous metals synthesis, dealloying and template deposition methods are the most commonly used and studied, whereas they are based on multistage technological processes and, as a rule, chemical etching, which can result in undesirable and uncontrollable changes of elemental composition and surface structure.

Unlike the above methods, we offer new technological approach of porous systems synthesis. It is based on steady-state condensation of substance under conditions close to thermodynamical equilibrium. Thus, when supersaturation of deposited vapours reduces to extremely low values, adatoms attach to a growth surface separately and only at active centres. Depending on constantly changing density of active centres, selective growth of structural fragments occurs. Partial joining of the structural fragments creates porous micro- and nanosystems.

We have realized this approach by means of specially designed and patented accumulative ion-plasma systems, based on modified magnetron sputterers [1]. These devices feature self-organization of extremely low steady-state supersaturation of deposited vapours in ultrapure inert ambient. As a result, we have fabricated porous metallic micro- and nanosystems with various architectures, such as: i) statistically homogeneous nanoislands with similar shape and size; ii) ordered nanoislands if using anodic aluminium oxide templates; iii) various highly porous three-dimensional structures; iv) systems of whiskers and nanowires (at prolonged deposition); v) porous columnar structures if applying negative bias.

We have performed preliminary tests of some of our three-dimensional aluminium and copper structures to check the possibility of infrared signal enhancing for *p*-NBA molecules and obtained enhancing factor of about 10 [2]. Further systematic measurements are needed.

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Metal-enhanced fluorescence of trimethine cyanine dyes bound to amyloid fibrils

V.B. Kovalska[1], **M.Yu. Losytskyy**[1], **Nuriye Akbay**[2], **S.V. Chernii**[1], **D.V. Kryvorotenko**[1],

S.M. Yarmoluk[1]

[1] *Institute of Molecular Biology and Genetics of NAS of Ukraine, Zabolotnogo Str. 150, Kyiv, 03680, Ukraine, E-mail: v.kovalska@gmail.com*

[2] *University of Namik Kemal, Tekirdag, Turkey*

Fibrillization of the native proteins i.e. formation of filamentous non-soluble amyloid aggregates is connected with the pathogenesis of neurodegenerative deceases such as Alzheimer's and Parkinson's ones. Thus development of the tools for the detection and study of these aggregates is of high importance, but only limited number of fluorescent probes (mostly Thioflavine T) is commonly used for this purpose. Recently we proposed trimethine cyanine dyes as amyloid sensitive probes [1], and supposed that these bind to β-pleated motifs of the fibrils.

The fluorescence intensity of the dye increases upon binding with fibrillar structures, but the value of the dye intensity is still moderate. Besides, amyloid fibrils detection should be performed in the low concentration range (due to the low solubility of fibrils), thus it is required to increase the "signal intensity".

These days metal enhanced fluorescence (MEF) is one of the most attractive topics to improve fluorescence intensity. Thus we have studied MEF of the dye in the presence of fibrillar protein on silver island films (SIF)-covered glass surface. All the surfaces were covered by PVP to increase the ability of proteins and dyes binding to surfaces. PVP-covered SIF and bare glass (for reference) surfaces were used for fluorescence emission measurements of the dye-fibrillar complex systems.

In the presented study MEF of a series of previously reported amyloid-sensitive trimethine cyanine dyes on SIF was studied. Fibrillar insulin was used as a model protein. Two of the dyes containing N,N'-alkylamino and N-alkylsulfo groups demonstrated enhancement in the fluorescence intensity up to 7 times on the SIF surfaces when compared with bare glass. Obtained results open the way for development of the MEF probes for the fibrillar structures detection.

This work was supported by The Scientific and Technological Research Council of Turkey (TUBITAK) Grant 114Z391 and NASU-TUBITAK joint project 114Z464.

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Studies of nonlinear optical properties for $Hg_3X_2Y_2$ (X = S, Se, Te; Y = F, Cl, Br, I) gyrotropic crystals

O.V. Bokotey, **I.P. Studenyak, I.I. Nebola**

Department of Applied Physics, Uzhhorod National University, Pidhirna Str., 46, Uzhhorod-88000, Ukraine, E-mail: bokotey_ov@ukr.net

Studies of $Hg_3X_2Y_2$ (X = S, Se, Te; Y = F, Cl, Br, I) crystals with corderoite structure represent scientific interest. It should be noted that they described by the $T^5 – J2_13$ space symmetry group that confirmed a presence of optical activity and electrooptical effect for this crystals which makes them perspective nanomaterials for nonlinear optics and optoelectronics. Besides that they characterize by such optical properties as photoconductivity, high refractive index and transparency in visible and IR-range. It is interesting of mention that the main structural feature of $Hg_3X_2Y_2$ mercury chalcogenhalogenides is the tendency to formation of various polymorphic modifications due to the great conformational capacity of mercury-chalcogen component. This features is promising when considering possible applications of these crystals. $Hg_3X_2Y_2$ crystals create new opportunities for design of new materials with promising properties.

The rotation dispersion gives information about the band structure and dispersion laws of valence and conduction bands. Optical activity effect represents a phenomenon which is one of the most sensitive to the structure features. The rotation of the polarization plane caused by specific interatomic interaction in compounds [1-2]. For analysis of interband transitions and their role in gyrotropy the detailed calculations of band structure of $Hg_3X_2Y_2$ (X = S, Se, Te; Y = F, Cl, Br, I) crystals were performed in the framework of DFT. Moreover the defective $Hg_3X_2Y_2$ crystals with various point defects (impurities, anion vacancies, vacancy-impurity complexes) have been simulated and analyzed by using the supercell model. The relation of the gyrotropy to the crystal structure and of its constituent elements to the energy levels (electronic, vibronic and vibrational) and to exciton effects have been discussed. Preliminary experimental study of absorption spectra edge indicates the presence of both direct and indirect optical transitions in the studied crystals. It should be noted that the main contribution to the rotation gives the direct interband transitions. According to our results of band structure calculations of $Hg_3X_2Y_2$ crystals a significant contribution to gyrotropy gives excitonic effects in the fundamental absorption edge.

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Plasmonic properties of gold trigonal and hexagonal nanoprisms deposited on the glass substrates

O.G. Lopatynska[1], A.M. Lopatynskyi[2], T.I. Borodinova[3], V.I. Chegel[2], L.V. Poperenko[1]

[1] *Faculty of Physics, Taras Shevchenko National University of Kyiv, Prospect Hlushkova, 4, Kyiv-03022, Ukraine.*
E-mail: olga_lopatynska@ukr.net

[2] *Department of optoelectronic functional transducers, V.E. Lashkaryov Institute of Semiconductor Physics NAS of Ukraine, Prospect Nauki, 41 Kyiv-03028, Ukaine.*

[3] *F.D. Ovcharenko Institute of Biocolloid Chemistry, NAS of Ukraine, Bulvar Acad. Vernadsky, 42, Kyiv-03680, Ukraine*

Metal nanocrystals are actual object for the modern biophysics mainly because of their usage in the sensors based on the localized surface plasmon resonance (LSPR) and as substrates for SEIRA and surface-enhanced Raman spectroscopy. Therefore, experimental investigation of their optical properties and their comparison with theoretical studies is an important task. Usually, for the theoretical consideration of the optical properties of plasmon-supporting nanoparticles Mie theory is used [1]. But it is applicable only for the spherical nanoparticles. For other nanoparticle shapes, different numerical methods of calculation are exploited. One of such methods is finite-difference time-domain technique. Its advantages and disadvantages are well described in [2]. So, the main aim of this research is investigation the optical properties of the gold trigonal and hexagonal nanoprisms, deposited on the glass substrates.

As a result, it was shown that for the studied structures the LSPR spectra depend on the crystals shape and size. The experimentally obtained and theoretically modeled LSPR positions differ from each other because of high spread of the shapes and sizes in the same sample and also because of aggregation effect of the nanocrystals which was confirmed by microscopy data.

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Temperature programmed desorption (TPD) mass spectrometry in surface chemistry studies of nanostructured systems

O.G. Obrazkov, V.O. Pokrovskiy

Laboratory for Mass Spectrometry of Nanosized Systems, O.O.Chuiko Insttitute of Surface Chemistry, Natl. Acad. of Sci. of Ukraine.17 Gen. Naumov Str., Kyiv 03164, Ukraine, E-mail: ucslnua@gmail.com

Temperature programmed desorption mass spectrometry (TPD MS) is one of the key analytical technologies on which the emerging mass spectrometric approaches are based. The equipment for TPD MS measurements includes vacuum system, controlled heater of the sample and the set of equipment for registration of volatile products in the process of sample decomposition and/or desorption of molecules adsorbed on the sample surface.

Similar to other temperature-programmed methods, in the case of TPD MS technique the sample is heated, usually by linear law. The temperature ramp rate do not exceed usually 10C/min to provide for the reliable identification of desorption and decomposition volatile products and for detailed tracing the kinetics of their evolution from the sample.

The apparatus for TPD MS measurements includes vacuum system, equipment for gas-phase modification and linear heating of the nanostructured sample, interface to mass spectrometer, an electron impact ion source, modified for TPD measurements, and also a set of computer programs for calculation and interpretation of kinetic parameters obtained in experiment. Pre-exponential factors and activation energies of thermally stimulated reactions are the most important parameters obtained in TPD MS experiment.

Thus, among the other methods of mass spectrometric analysis, the TPD MS is one of the most promising approaches to investigation of processes occurring with biomolecules in the surface area of nanostructured samples. The evolution of volatile desorption products and their destruction occurs in quazi-stationary conditions, providing for obtaining of reliable information concerning reaction orders, activation energies and pre-exponential factors of reactions, in particular of biologically active molecules, on nanostructured surfaces.

TPD MS approach is most efficient being combined with laser desorption ionization mass spectrometry (LDI MS) in studies of biomolecules adsorbed on nanostructured surfaces, in particular for biophysical, biological and medical applications.

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The laser desorption mass spectrometry in biomedical studies

V.O. Pokrovskiy, O.G. Obrazkov

Laboratory for Mass Spectrometry of Nanosized Systems, O.O.Chuiko Insttitute of Surface Chemistry, Natl. Acad. of Sci. of Ukraine.17 Gen. Naumov Str., Kyiv 03164, Ukraine, E-mail: ucslnua@gmail.com

Laser desorption ionization mass spectrometry (LDI MS) is one of the key analytical technologies on which the emerging MS approaches are based. It may provide for detection and quantization of thousands of proteins and biologically active metabolites from a tissue, body fluid or cell culture working in a ‘‘global’’ or ‘‘targeted’’ manner, down to ultra-trace levels. It can be expected that the high performance of MS technology, coupled to routine data handling, will soon bring fruit in the request for a better understanding of human diseases, leading to new molecular biomarkers, hence affecting drug targets and therapies. Here we focus on the main advances in the MS technologies, influencing genomics, transcriptomics, proteomics, lipidomics and metabolomics fields.

Genomics. Cognitive genomics examines the changes in cognitive processes associated with genetic profiles. Comparative genomics: Study of the relationship of genome structure and function across different biological species or strains. Functional genomics: Describes gene and protein functions and interactions (uses microarray kind of techniques). Metagenomics: Study of metagenomes, i.e., genetic material recovered directly from environmental samples. Personal genomics. Branch of genomics concerned with the sequencing and analysis of the genome of an individual. Once the genotypes are known, the individual's genotype can be compared with the published literature to determine likelihood of trait expression and disease risk. Epigenomics: Study of the complete set of epigenetic modifications on the genetic material of a cell, known as the epigenome.

Lipidomics. Lipidome is the entire complement of cellular lipids, including the modify-cations made to a particular set of lipids, produced by an organism or system. Lipidomics is a large-scale study of pathways and networks of lipids and laser desorption mass spectrometry techniques are efficiently used.

Proteomics. Large-scale study of proteins, particularly their structures and functions. Mass spectrometry techniques are used. Immunoproteomics: study of large sets of proteins (proteomics) involved in the immune response

Transcriptomics. Study of transcriptomes, their structures and functions. Scientific study of chemical processes involving metabolites.

Thus, the Laser Desorption Mass Spectrometry (LDI MS) already plays essential role in modern biological and medical studies. The new integrated approaches using LDI MS are expected to contribute in the development of nanobiophysics and personalized medicine for health monitoring and prevention.

Session 4:

Interactions of biomolecules with the nanoparticles and nanostructured surfaces

Glyconanoparticles of noble metals for cancer therapy direct use

V.R. Estrela – Llopis[1], A.V. Chevychalova[1], O.M. Fesenko[2], P.M. Litvin[3],

V.R. Romanuk[3], L.M. Skivka[4]

[1] F.D. Ovcharenko Instityte of Biocoloid Chemestry, NAS of Ukraine, blvd. Vernadskogo, 42, Kiev-03142, Ukraine. E-mail: victorio.estrela@gmail.com

[2]Institute of Physics, NAS of Ukraine. Prospect Nauki, 46, Kiev-03039, Ukraine.

[3] V. Lashkarev Institute of Semiconductor Physics, NAS of Ukraine, Prospect Nauki, 41, Kiev-03028, Ukraine.

[4] Biological Faculty of T.Shevchenko National University of Kiev, Glushkov Avenue 2, Kiev-022, Ukraine.

The results of studies of the interaction of gold, platinum and silver nanoparticles (NPs) obtected by adsorption layer of anionic polysaccharides (PS) of microalgae Chlorella vulgaris with cells of blood cancer (line Jurkat, Namalwa, compared to healthy lymphocytes), ovarian cancer cells line A2780 and Ehrlich ascites carcinoma are presented..

It was shown that the initial nanoparticles, and independently of, polysaccharides have a weak cytotoxic effects at low concentrations used to obtain NP-PS. However, bioconjugates NP-PS show selective, relatively fast and strong toxic effect on cancer cells.

The mechanisms of the influence of PS on the aggregation of the bioconjugates NP-PS with cells, their penetration (endocytosis), localization in the cell and the role of PS conformation in above processes are discussed. The results of researches of 1) physical properties of the nanoparticles (TEM, AFM, UV-IR, SEIRA spectroscopy, microelectrophoresis); 2) heterocoagulation with cells, the kinetics of this process and kinetics of the corresponding cytotoxic effect; 3) biochemical analysis of the NP-PS toxic effect's causes (MTT and ROS assay,TEM) are presented

Represented results show that the surface modification of investigated nanoparticles by acidic high molecular polysaccharides leads to toxic and selective effect on cancer cells. This determines the good prospects for creation NP-PS pharmaceutical preparations of the direct action for the cancer medicine.

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Novel prospective nanomaterials for fluorescence sensing and Imaging

Alexander Demchenko, Volodymyr Nazarenko, Mykola Kaniuk, Kyrylo Pyrshev,
Mariia Dekaliuk, Ihor Panas

Palladin Institute of Biochemistry, Laboratory of Nanobiotechnology, Kiev 01030, Ukraine
E-mail: alexdem@ukr.net

Modern biophysics research on molecular and cellular level requires creating novel fluorescent (luminescent) nanomaterials with the properties superior to that of traditionally used organic dyes. They are semiconductor quantum dots, up-converting nanocrystals, fluorescent carbon nanostructures and also conjugated polymers as well as the dye-doped nanoparticles and dendrimers. With dramatically higher absorbance, increased photostability and the ability of superquenching they increase the brightness of images and extend the possibilities of fluorescence sensing. Still, they lack important features of organic dyes - the ability of responding to different intermolecular perturbations by spectral shifts or generation of new bands in emission or by changes in anisotropy and lifetime. Intrinsic heterogeneity of their structures and not always clear mechanism of their response complicate their active use.

However, many elegant ways in application of novel fluorescent emitters appear when organic and inorganic structures are assembled into nanocomposites. They can be transformed into smart nanoscale instruments with advanced functions: (a) *Wavelength converting*, the shifting of emission bands in the entire visible and near-IR range. This can be achieved by assembling efficient donors and acceptors participating in transfer of electronic excitation energy via “cascades”. (b) *Light harvesting*. This is achieved by transferring the excitation energy of a large number of spectrally distributed fluorophores to small number of selected fluorophores resulting in the bright emission of the latter. (c) *Lifetime engineering* in fluorophores serving as excited-state energy transfer acceptors if they are excited via the donors with longer lifetimes of emission. In this way the emission lifetime can be extended by several orders of magnitude shifting to microsecond-millisecond time range. (d) *Superquenching*, which is the effect of total quenching of fluorescence of all fluorophores in a nanocomposite when one of them interacts with the quencher. (e) *Plasmonic enhancement*, resulting from resonance effect of interaction of excited fluorophore with nanoparticles of noble metals, generating localized plasmons. Under the influence of their local electromagnetic fields, the two coupled effects of increasing the absorption cross-section and enhancing the fluorescence quantum yield increase dramatically the brightness of light emitters.

Thus, assembly of fluorescence emitters into nanocomposites allows achieving very important functions that are not observed in separate emitters alone. Since all types of fluorescent molecules and nanoparticles can be combined in nanocomposites, these new features can be realized in immense number of ways. Such possibilities are demonstrated based on results of recent work of our laboratory. We synthesized and applied in fluorescence imaging of living cells the nanoclusters composed of organic dyes and metal cations, carbon nanomaterials (C-dots) of different composition, the wavelength-switching polymeric materials and nanocomposites that combine fluorescent and magnetic properties.

Conductometric enzyme biosensors

S.V. Dzyadevych[1,2], **A.P. Soldatkin**[1,2]

[1] *Laboratory of Biomolecular Electronics, Institute of Molecular Biology and Genetics, Natl. Acad. of Sci. of Ukraine. 150 Zabolotnogo St., Kyiv 03680, Ukraine, e-mail:* dzyad@yahoo.com

[2]*Institute of High Technologies, Taras Shevchenko Kyiv National University, 64 Volodymyrska St., Kyiv 01003, Ukraine*

During recent decades there has been shown unprecedented interest in the development of analytical devices for the detection, quantification and monitoring of different biological and chemical compounds. The presentation is a review of own 25 years of research concerning the development of conductometric enzyme biosensors for direct substrates or inhibitors analysis. The biosensors were designed by using immobilised enzyme and interdigitated planar electrodes. Highly specific, sensitive, simple, fast and cheap determination of different substances renders them as promising tools foe needs of medicine, biotechnology, environmental control, agriculture and food industry.

The conductometric biosensors for quantitative determination of different substrates (glucose, urea, sucrose, lactose, maltose, arginine, etc.) have been developed and their laboratory prototypes were fabricated. Improvement of analytical characteristics of such biosensors may be achieved using nanoparticles of different nature, differential mode of measurements, working solution with different buffer concentrations and specific chemical agents, charged additional membranes, etc. These approaches allow one to decrease the effect of the buffer capacity influence on the sensor response in an aim to increase the sensitivity of the biosensors and to extend their dynamic ranges.

The biosensors for analysis of toxic substances such as organophosphorous and carbamate pesticides, heavy metal ions and aflatoxins have been designed on the basis of enzyme inhibition effect. The conception of a multisensor for toxic substances is developed. The respective advantages and disadvantages of developed biosensors as well as possibility of practical application of such biosensors will be discussed.

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Nanosized zicrconia/oligomeric shell: influence of zirconia surface

O. Gorban[1], N. Mitina[2], N. Bukartyk[2], S. Gorban[1], O. Shevchuk[2],

A. Zaichenko[2], T. Konstantinova[1]

[1] Department of Materials Science and Engineering, Donetsk Institute for Physics & Engineering NAS of Ukraine, Prospect Nauki, 46, Kiev-03039, Ukraine.

E-mail: matscidep@aim.com

[2] Lviv Polytechnic National University , S. Bandera St,, 12, Lviv, Ukraine

E-mail: zaichenk@polynet.lviv.ua

Nanocomposites consisting of mineral core and polymeric shell are the most promising for using in polymeric chemistry, biological and medical application, for instance, for labeling pathological cells. The main interesting for these goals are Y doped ZrO_2 nanoparticles (NPs) due to complex of their unique properties and biological tolerance. The functionalization of zirconia surface gives it new properties, there are the formation of task-oriented reactivity ability of NPs surface. The main moment at construction of core/shell structure is provided the compatibility between polymeric matrix and NPs. The properties of the NPs are defined by their size, structure and surface properties depending on synthesis conditions, such as annealing temperature of NPs. Thus the formation of Y doped ZrO_2 in the range 300-1000^{o}C passes by loss a chemically and physically bound water, a creation and a closing cationic and anionic vacancies that changes the acid-base state of the surface, its charge, and the reactivity of the particles to the polymer. In this work, novel route for creation of reactive shell on surface of ZrO2 NPs possessing tailored compatibility to polymer matrix was successfully tested. It was shown, surface state influences on the amount of adsorbed OMC on the nanoparticles surface. The variation of annealing temperature allows producing nanopowders of different size and surface states. The Y doped ZrO_2 NPs surface contains active acidic and basic sizes of Brensted nature. It was shown, that ratio between amount of basic and acidic Brensted sizes is no monotonically on average NPs size. The change of zeta potential of NPs from its size also exhibit similar behavior. The minimum of these values is observed at NPs size of 24 nm. NPs of such size is formed by annealing of 900°C. This temperature is critical above of the temperature the diffusion yttrium and zirconium will begin and oxygen diffusion is began more intensity. It can say, different mechanisms of surface forming are for Nps synthesized below and above this temperature. For NPs system with annealing temperature of 900^{o}C the interaction of OMC with NPs surface possible leads to formation of thermodynamically stable complex NPs– OMC polymer, and further sorption of OMC don't occur. The latest nanopowders are best for creation of composite structure of core/shell type. Mechanisms of interaction are discussed.

Harmonic Nanoparticles – Biolabeling Based on Nonlinear Optical Approach

V.Ya. Gayvoronksy[1], **R.Le Dantec**[2]

[1] *Department of Nonlinear Optics, Institute of Physics NAS of Ukraine. Pr. Nauki, 46, Kiev 03680, Ukraine.*
E-mail: vlad@iop.kiev.ua
[2] *SYMME, Universite de Savoie, BP 80439, 74944 Annecy Le Vieux Cedex, France*

The invention of multi-photon microscopy in 90th has revolutionized the field of optical imaging. A new milestone has been reached, thanks to the availability of compact ultrafast laser sources and covering the spectral range up to 1300 nm. In the last years a new approach have been introduced based on inorganic nanocrystals with non-centrosymmetric lattice, **harmonic nanoparticles (**HNP) **[**1**,** 2] such as $BaTiO_3$ or $LiNbO_3$. By their crystalline structure, HNPs present **very efficient quadratic nonlinear optical response** [3], and can be effectively imaged using second harmonic generation (SHG) as contrast mechanism. Being smaller than coherence wavelength, no phase-matching limitations apply and they efficiently respond to excitation from the UV to the mid-IR. Moreover their signal is not bleaching, blinking, nor saturating because of the non-resonant character of the parametric interaction mechanism.

A new microscopy techniques based on bright, stable and multifunctional contrast agents that combine high penetration depth and large field of view are needed to better elucidate living processes that govern metabolism and disease mechanisms. HNPs have already proven to be excellent candidates to fully exploit the potential of multiphoton imaging. The complete absence of bleaching and blinking, and their narrow emission bands are among the key properties of these inherent nonlinear optical probes.

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ELECTRONIC EXCITATION ENERGY TRANSFER IN BIOPOLYMERS.

Valeriy M. Yashchuk

Kyiv Taras Shevchenko University, 60 Volodymyrska Str., 01601, Kyiv, Ukraine
yashchukvaleriy@gmail.com

The optical properties of biomolecules are determined mainly by molecular fragments containing -electron systems similar as that takes place in synthetic organic compounds. The weak interaction of these systems of neighbor fragments (f.e. polymer cells) leads to delocalization in them the electronic excitations (appeared due to light absorption or penetrated radiation) and their transfer to so-called excitonic traps or guest molecules.

In our presentation the processes of electronic excitation energy transfer (EEET) in biomacromolecules are examined. The results on EEET in DNA, RNA and some proteins are presented and discussed The effect of EEET on fluorescence, phosphorescence and delayed fluorescence of biomacromolecules and their functional fragments (including telomers) and more complicate bioobjects such as viruses are examined.

Zirconia biomaterials for medicine

I.A. Danilenko[1], T.E. Konstantinova[1], S.V. Sokhan[2], O.I. Hodovana[3]

[1] Material Science Department of Donetsk Institute for Physics and Engineering named after O.O. Galkin NAS of Ukraine. Prospect Nauki, 46, Kiev-03039, Ukraine.
E-mail: matsidep@aim.com

[2] V. Bakul Institute of Superhard Materials NAS of Ukraine. 2, Avtozavodskaya Str., Kiev, 04074
E-mail: sokhan@ism.kiev.ua

[3]Danylo Halytskyi Lviv National Medical University, Department of Therapeutic Dentistry Post-Diploma Education. Pekarska Str. 69, 79010, Lviv, Ukraine,
E-mail: ohodovana@gmail.com

Zirconia nanomaterials proved their efficacy in a reparative medicine, since it has been shown that they possess considerable mechanical strength, flexibility, and are chemically stability. Zirconia ceramics are widely known as biocompatible materials for dental prosthesis and hip joint replacements. Zirconia powders are used as fillers for osteoplastic polymer based materials. The main primary idea of such various applications is producing the separated nanoparticles with specially modified surface which has been adopted for different aims.

The method of powder preparation is based on chemical precipitation method and allows obtaining the nanopowders with a wide range of particles sizes and surface area. The process of surface modification can be consisting from physical or chemical actions. Preparation of porous or dense ceramics materials can be easy realized by CAD/CAM technology and sintering.

The several examples of different types of zirconia materials prepared from nanopowder and results of their testing for biocompatibility and wear will be shown (fig.1).

Fig.1 – Examples of zirconia applications

Factors ruling the adsorption of proteins on silica nanoparticles, spectroscopic investigation of the interface events and their influence on cell uptake

F. Catalano[1], **G. Alberto**[1], **L. Accomasso**[2], **C. Giachino**[2] **and G. Martra**[1]

[1]*Department of Chemistry and NIS Centre of Excellence, University of Torino, via P. Giuria 7, 10125 Turin, Italy, E-mail: federico.catalano@unito.it*

[2]*Department of Clinical and Biological Sciences, Regione Gonzole 10, 10043 Orbassano (Turin), Italy*

What cells “see” when are contacted with nanoparticles? The correct answer must consider the formation of an hybrid solid/protein interface, that could also result in the formation of a “corona” layer [1]. As for biomaterials, also for nanoparticles, the nature of the biological responses is determined by the proteins adsorbing on the material surface immediately after the contact with physiological environments. In this work, the quantitative and structural aspects of the adsorption, of both a single model protein (Bovine Serum Albumin, BSA) in buffered solutions and a complex protein pool (Fetal Bovine Serum, FBS) in cell culture media, on fluorescent silica nanoparticles (NPs) were investigated

In order to quantitatively asses the covering degree, the surface area actually available for protein adsorption was determined by studying the agglomeration state of NPs when suspended at physiological pH in both presence and absence of proteins (Dyamic Light Scattering).

Electronic spectroscopy analyses (UV-Vis and Circular Dichroism), and measures of the silica surface charge (ς-potential) after contact with proteins, provided additional information not only on the degree of nanoparticles surface coverage but also on the conformational changes involving the structure of adsorbed proteins.

Briefly, differently from BSA in buffered solutions, NPs incubation with FBS in culture medium, results in the formation of a complete corona layer even at the lowest considered FBS concentration. Noticeably, cell tests (monitored by fluorescence confocal microscopy), where mesenchymal stem cells were contacted with NPs with different FBS concentrations in the culture medium, revealed that the presence/absence of proteins have higher influence on the rate and the amount of NPs uptake with respect to the degree of surface coverage.

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Vibration spectra of DNA in confined volume of photonic crystal

V.V. Boiko, **O.P. Gnatyuk, G.I. Dovbeshko**

Department of Physics of Biological Systems, Institute of Physics, Natl. Acad. of Sci. of Ukraine. Prospect Nauki, 46, Kyiv-03680, Ukraine.

E-mail: vb@iop.kiev.ua

Usage of 2D [1] and 3D [2] photonic crystals (PC) as substrates for registration of fluorescent images of biological molecules is a promising area of the fluorescence microscopy. However, it is important to identify the changes in structure (conformation) of biological molecules after their placement into confined volume of 3D PCs. IR spectra of DNA after infiltration into the pores of 3D PCs has been analysed in the work [3]. Here we present the Raman spectra of DNA infiltrated in the pores of PCs.

The DNA has three main canonical forms: A, B and Z. It is known that DNA in the cell has predominantly B or B-A forms. These forms could changed under biochemical processes. Raman marker bands of DNA are: B-form - 681, 787, 834 and 1376 cm^{-1}; A-form - 663, 781, 806, 1373 cm^{-1}; Z-form - 625, 748, 810, 1264 cm^{-1}. We registered the shifts of marker bands, redistribution of their intensity, the appearance of new bands belonging to vibrational modes of sugar-phosfate backbone and nucleosides. This indicates a change of DNA conformational states upon its infiltration in the pores of PCs. We have registered an increase of intensity of the bands at 475 cm^{-1} along with a shift of the band at 768 cm^{-1} which indicates a distortion of the DNA backbone in thymine sites. We registered a decrease of intensity of the band of nucleobases at 1570 cm^{-1} (guanine, adenine) and at 1659 cm^{-1} (thymine, guanine, cytosine) in the Raman spectrum of DNA infiltrated in the PC. The appearance of intense bands at 1454 cm^{-1} (CH_2) and 1463 cm^{-1} (CH_3) indicates a distortion of backbone and change of location of these groups in comparison with those in canonical DNA forms. Increase of intensity of the C-H stretching vibrations in the region of 2860-3000 cm^{-1} by 4 times and redistribution of the bands of CH_2 and CH_3 groups has been registered

We demonstrate that introduction of DNA into the pores of PC leads to the changes in its conformation due to the effects of confinement in limited volume. The content of A and Z forms as well as undefined conformational states increases upon infiltration into PC.

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The electronic spectra of copper nanoparticles - ceftriaxone conjugate

D.O. Kovalova[1], O.P. Dmytrenko[1], M.P. Kulish[1], T.O. Busko[1], O.L. Pavlenko[1], P.V. Simanov[2], I.S. Chekman[2], N. Vityuk[3]

[1]Taras Shevchenko National University of Kyiv, Faculty of Physics, 64/13 Volodymyrska str., 01601, Kyiv, Ukraine.
E-mail: kovaloyvadaria@mail.ru
[2]Bogomolets National Medical University, Kyiv, Ukraine, 34, Prospekt Peremohy, 02000, Kyiv, Ukraine.
[3]Chuiko Institute of Surface Chemistry, NASU, 17 Generla Naumova Street, 03164, Kyiv, Ukraine.

Ceftriaxone is one of the effective bactericidal antibiotics used in modern medicine. But there is a tendency to reduce the effectiveness of Ceftriaxone therapy because of the emergence of insensitive bacteria. There are evidences of the conjugation of drugs to nanoparticles enhances their potency.

The interaction between copper nanoparticles and Conjugate of copper nanoparticles with Ceftriaxone were investigated by the optical spectroscopy and quantum-chemical calculations. Also we have investigated the interaction with peptides, lipids and carbohydrate components of the bacteria cell wall.

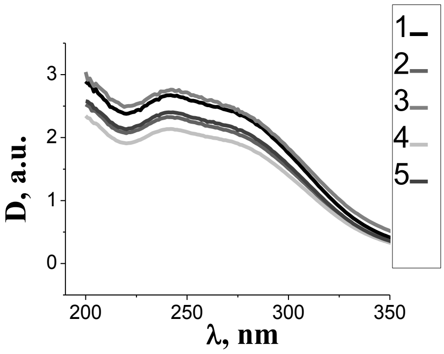


Fig.1. The UV - vis spectra of Conjugat of copper nanoparticles with Ceftriaxone (4) and Conjugat of copper nanoparticles with Ceftriaxone with: Alanine (1), glycine (2), glutamic acid (3), lysine (5)

Most probable that the antibacterial action of Conjugat of copper nanoparticles with Ceftriaxone for the cell membrane occurs due to interaction with a glutamic acid and lysine.

Coherent anti-Stokes Raman scattering (CARS) and imaging of DNA molecules

Denys Pidhirnyi[1], Galyna Dovbeshko[1], Andrej Dementjev[2], Evgeniya Kovalska[3]

[1] *Institute of Physics, National Academy of Sciences of Ukraine, 46 Nauki Ave, Kyiv 03680, Ukraine*
[2] *Institute of Physics, Center for Physical Sciences and Technology, A. Goštauto 11, Vilnius LT-01108, Lithuania.*
[3] *Department of physics, Bilkent University, 06800, Ankara, Turkey*

DNA molecules are of great interest for biochemical application that is why imaging of DNA molecules is important. Here we apply one of the most sensitive imaging method, namely, Coherent anti-Stokes Raman scattering (CARS) microscopy.

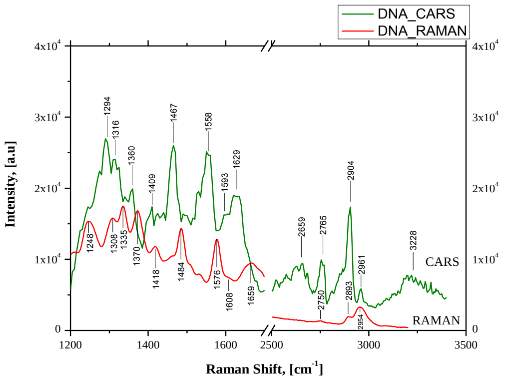
It is known an advantage of this method for imaging of biological molecules and cells. We wanted to enhance a contrast of imaging and sensitivity of vibrational spectroscopy using graphene layers as substrate.

Along with a great sensitivity of vibrational spectroscopy: Infrared (IR), Raman scattering (RS), to conformational states of DNA, determination of DNA interaction with ligands, CARS spectroscopy in contrast to microscopy has some disadvantages: complex bands in CARS, big amounts of substances, etc. That is why CARS spectroscopy is not used as conventional spectroscopic method.

In RS and IR spectroscopy we need concentration of solution about units of mg/ml of DNA, (for SERS spectroscopy about 2 order less). For CARS spectroscopy, in which $I \sim m^2$ ($I \sim m$ for RS) we need more substance in probe than in RS.

So, CARS spectra of DNA are not studied. We got CARS spectra of DNA and compare them with RS. CARS spectrum was of good quality for DNA about 40 mg/ml, for 2 mg/ml we got recognizable spectra of not good quality. In the case of 2 mg/ml we got good spectra in conventional Raman spectroscopy.

In all cases we used for Raman spectroscopy a metal substrate. In the case of CARS a single layer of graphene was used as a substrate. We wanted: 1) to enhance scattering signal from DNA and 2) to get DNA imaging.



We did not enhanced CARS signal from DNA molecule on graphene substrate in contrast to other type of substrates. However we got imaging from DNA of small quality when spectra is not registered, due to contrast between DNA and irradiated graphene surface that emitted a radiation (multiphoton luminescence and non-resonance CARS) in near IR and visible region. For DNA molecules in the 1200-1700 cm^{-1} and 2800-3000 cm^{-1} range we have registered a number of lines of big intensity with resolved structure which we compare with Raman spectra and assigned to proper molecular groups. The bands registered in FCARS mode have non-resonant components. In the 2400-3400 cm^{-1} DNA shows the spectra similar to spectra of their components (Thy and /or Ade) with the main contribution of CH, NH, OH vibrations. A characteristic feature of CARS spectra: 1) low frequency shift about 10 cm^{-1} in comparison with conventional RS; 2) a similarity of PCARS an FCARS spectra. In both spectral regions we got imaging of DNA on the graphene surfaces with and without obtaining the spectra.

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Simulation of protonated nitrogen bases interactions with carbon nanotubes

V.G. Zobnina, M.V. Kosevich, V.S. Shelkovsky, S.G. Stepanian,
V.A. Karachevtsev

[1] *Department of Molecular Biophysics, B. Verkin Institute for Low Temperature Physics and Engineering of the National Academy of Sciences of Ukraine,*
Lenin Avenue, 47, Kharkov-61103, Ukraine, E-mail: Zobnina@ilt.kharkov.ua

Control of the charge state of biomolecules, DNA and its components in particular, in bionanocomposites is promising for operation of bionanodevices. Charge of nucleic acid nitrogen bases can be changed by protonation under proper conditions [1].

In the present work we report computer simulation of complexes of carbon nanotube (CNT, zigzag (10,0) fragment) with protonated cytosine (Cyt•H^+) and adenine (Ade•H^+) by means of quantum chemical calculations performed with M05-2X/6-31G* for CNT and M05-2X/6-31++G** for nitrogen bases.

Predictably, formation of stable complexes of the protonated bases with CNT was observed and the interaction energy of the charged species with CNT was higher than that with the neutral ones reported earlier in [2]: -139.1 kJ•mol^{-1} for CNT•Cyt•H^+ *vs* -50.3 kJ•mol^{-1} for CNT•Cyt and -139.0 kJ•mol^{-1} for CNT•Ade•H^+ *vs* -59.0 kJ•mol^{-1} for CNT•Ade. The main emphasis in the data analysis was made on the distribution of the electrostatic potential over the complexes. Positive potential smeared around a single protonated base on the complex formation provided a volume of delocalized positive potential around the whole complex. A procedure of calculation the difference between the maps of electrostatic potentials of the whole complex and the protonated base was proposed; the result had revealed polarization of the CNT at the site of the cation attachment, namely formation of a zone of negative potential.

Thus, protonation of nitrogen bases under the relevant condition may enhance the stability of the CNT composites with nucleic acids.

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FTIR spectroscopy study of BN nanoparticles interaction with cancer cells

O.P. Gnatyuk[1], G.I. Dovbeshko[1], O.Yu. Posudievsky[2], A. Yershov[3]

[1] *Department of Physics of Biological Systems, Institute of Physics, Natl. Acad. of Sci. of Ukraine. Prospect Nauki, 46, Kiev-03039, Ukraine.*
E-mail: hrysantemka@ukr.net
[2] *L.V. Pisarzhevsky Institute of Physical Chemistry, Natl. Acad. of Sci. of Ukraine, Prospect Nauki 31, , Kyiv-03028, Ukraine*
[3] *Institute of Molecular Biology and Genetics, Natl. Acad. of Sci. of Ukraine., 150 Zabolotnogo Str., Kyiv-03680, Ukraine.*

It is known that boron nitride (BN) nanoparticles are non-toxic and could be modified with different functional groups, including anticancer drugs. In this work an amplification of anticancer drugs efficiency by BN nanoparticles was studied.

The LNCaP strains of cancer cells were cultivated under standard conditions (DMEM, 10% FBS, in an atmosphere of 5% CO_2). The next day BN nanoparticles with concentration of 0.9 mg/mL were added to the dishes with cancer cells and the cells with BN were cultivated during 1, 2 and 10 hours respectively. Then the cells were washed, deposited on Au substrate of 0.4 nm thickness and liophilically dried. SEIRA spectra were collected in 5300–400 cm^{-1} range using IFS 66 Bruker spectrometer at transmittance mode. After measuring the FTIR spectra the bands were deconvoluted using the Opus-4.2 program.

The results of the study of IR absorption spectra of the LNCaP strains of cancer cells show that main changes occur in the region of symmetric vibration of PO_2^- (the band about 1085 cm^{-1}, redistribution of the band components) and in the region of hydrogen bonds (the band about 3300 cm^{-1}, widening of this band with redistribution of components). The obtained results allowed us to conclude that BN nanoparticles pass through cell membrane and are located close to the nucleus of the cells.

The peculiarities of interaction of the BN nanoparticles with the cancer cells are discussed.

The investigation of interaction between oxyresveratrol and fullerenes in the aqua solutions

M. O. Kuzmenko[1*], **P. V. Petrenko**[1], **M. A. Zabolotnyi**[1], **O.P.Dmetrenko**[1], **N.P. Kulish**[1]

[1]Faculty of Physics, Taras Shevchenko National University of Kyiv, Acad. Hlushkov Ave., 4, Kyiv, Ukraine
E-mail: kuzjamaryna@gmail.com

In the recent years, oxyresveratrol has attracted considerable interest for its beneficial effects for human health: cardiovascular protective effects, anti-inflammatory properties, platelet anti-aggregate and antitumor activity. It is know that the nanostructure modification of drugs can reduce cytotoxic effects and can be used for targeted cancer therapy.

The possibility of formation charge-transfer complexes between the molecules of oxyresveratrol and fullerenes(C60,C70), the existence of their interaction have been proved using small angles neutron scattering, Surface-enhanced Raman scattering spectroscopy, infrared absorption spectroscopy and UV spectroscopy (Fig1). The electronic parameters of the oxyresveratrol and its complexes will be defined using Gaussian 03.

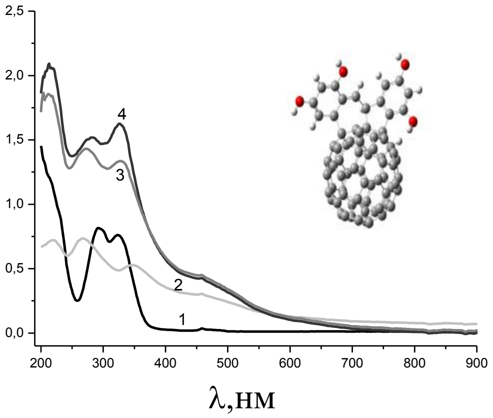

Fig.1. UV spectra of 1- oxyresveratrol (oxy) soluble on water, 2-fullerene aqua solutions (FAS C60); 3- C60: oxy as 1:2; 4- C60: oxy as 1:3

Magnetic and fluorescent bifunctional nanocomposites for biomedical application

Ihor Panas and Alexander Demchenko

Palladin Institute of Biochemistry, Laboratory of Nanobiotechnology, Kiev 01030, Ukraine
E-mail: i.d.panas@gmail.com

Nanomaterials with multifunctional properties are in great demand due to their outstanding characteristics and wide range of possible applications. Meantime, magnetic nanoparticles such as of iron oxide by their own do not possess much useful features for biological and medical application and for their efficient use require further modifications. Encapsulation into the inert shell, doping with fluorescent dyes and coupling with biological molecules (antibodies, ligands, etc.) may result in appearance of versatile and valuable nanodevices. Such products are in great importance for biological imaging, cell tracking, magnetic bioseparation and drug delivery techniques. Regulation of cellular activities in controlled manner by applying magnetic field is unique and promising tool which also becomes possible due to magnetic nanocomposites allowing both fluorescence and NMR imaging. On cellular level they are expected to become valuable tools in complex study of membrane receptors' functions and their lipid surroundings. For this purpose we synthesized novel multifunctional nanocomposites composed of superparamagnetic core of iron oxide and inert shell of silica functionalized with amino groups. Amino groups on surface make them ready for conjugation with different ligands including proteins via routine methods. Labeling by fluorescent molecules allows applying different methods of optical spectroscopy and microscopy.

There are plenty of routes for magnetic core synthesis. However, decomposition of metal-organic precursor was chosen as the most efficient, convenient and reliable. At high temperature conditions (about 260 °C) with triethylene glycol as solvent an iron (III) acetylacetonate decomposes with iron oxide nanocrystals formation. Triethylene glycol functions of both reducing agent and solvent. Microwave-assisted heating was applied as fast and efficient method compared with conventional heating. Outer silica layer was synthesized by Stöber process. Notably, both core and shell synthesis provides a control over particle size that allows optimizing it in broad ranges.

Designed nanoparticles are of significant value for both applied and fundamental aspects of biological and/or medical research, particularly on cellular level. Magnetic separation of cell cultures under optical control with elimination of dead cells or of malignant stem cells may become possible based on interaction of designed nanocomposites with specific cell receptors.

Session 5:

Hybrides of the biomolecules with carbon nanostrucrures

Influence of Amino Acid Doping On Photoluminescence Intensity From Semiconducting Carbon Nanotubes

N.V. Kurnosov[1], **V.S. Leontiev**[1], **V.A. Karachevtsev**[1]

[1] *B. Verkin Institute for Low Temperature Physics and Engineering, 47 Lenin Ave., 61103 Kharkov, Ukraine, E-mail: N. Kurnosov@ilt.kharkov.ua*

Quantitative analysis of amino acid levels in the human plasma or urine is important for the investigation of cellular functions and for the early clinical diagnosis of a variety of diseases. Such amino acid as cysteine is widely distributed in biological tissues and plays a central role in protein synthesis, detoxification and metabolism. Among many possible sensing methods fluorescence detection offers certain advantages such as high sensitivity, simplicity of implementation, and an ability to allow the real-time monitoring.

In the present work we study the influence of doping with thirteen amino acids (cysteine, glycine, alanine, lysine, aspartic acid, proline, arginine, histidine, methionine, serine, asparagine, valine, phenylalanine) on nanotube PL. PL spectra of semiconducting SWNTs in aqueous suspension with DNA were observed in the range of 1.1-1.6 eV (excitation was performed with green laser, λ_{ex}=532 nm, 5 mW). Each amino acid was added separately into portion of nanotube suspension. The largest PL enhancement was found after cysteine doping (up to 17 % at 10^{-4} mol L^{-1} concentration) [1]. The absence of the spectral shift of bands in the nanotubes NIR absorption spectrum after cysteine doping indicates that this doping has a weak influence on the polymer coverage of nanotubes in aqueous suspension. Most likely, the PL intensity increases due to the passivation of p-defects on the nanotube sidewall by the cysteine molecules containing reactive thiol group. The effect of doping with other amino acids without this group on the PL intensity is essentially weaker (the PL enhancement does not exceed 4%). It is important to note that amino acids studied belong to different subgroups and two of them (serine and methionine) are structurally very close to cysteine. So, presence of redox - active thiol group in cysteine structure is crucial for its influence on nanotube PL.

We have also studied the effect of several external factors on the cysteine-induced enhancement of PL from nanotubes covered with DNA: weight ratio between nanotubes and DNA before suspension preparation, type of sonication treatment of the suspension (tip or bath), the ionic strength and pH of aqueous suspension, UV irradiation of suspension.

20. *Kurnosov N.V., Leontiev V.S., Linnik A.S., Karachevtsev V.A.* Influence of cysteine doping on photoluminescence intensity from semiconducting single-walled carbon nanotubes // Phys. Chem. Lett.-2015.**-623,-**P. 51-54.

Noncovalent interaction of heterocyclic organic molecules with graphene: DFT study

E.S. Zarudnev, S.G. Stepanian, V. A. Karachevtsev

B.I. Verkin Institute for Low Temperature Physics and Engineering, Natl. Acad. of Sci. of Ukraine. 47 Lenin ave., Kharkov, 61103, Ukraine, E-mail: zarudnev@ilt.kharkov.ua

Noncovalent functionalization of graphene and interactions with biomolecules, which do not disrupt the extended π-conjugation on the graphene surface, unlike covalent functionalization open a gateway to new fields in biotechnology. In this work the structure of hybrids formed by heterocyclic compounds such as imidazophenazine (F1) and its derivatives (2-methylimidazo-[4,5-d]-phenazine (F2), 2-trifluoridemethylimidazo-[4,5-d]-phenazine (F3), and 1,2,3-triazole-[4,5-d]-phenazine (F4)) with graphene and noncovalent interactions between the components were studied employing the quantum-chemical calculations. Note that spectral properties of imidazophenazine and its deriviates are exploited in DNA study. The interaction energy and structure of imidazophenazine and its derivatives with graphene was compared with those determined for graphene hybrid with tetracene. The geometries of the complexes formed by graphene sheet with tetracene and F1-F4 compounds were optimized at the DFT level of theory using the M05-2X functional. Upon calculations, the molecules studied were located on graphene along two directions: zigzag and armchair ones. It was revealed that tetracene as a symmetrical molecule shows a small difference in the binding energy with graphene along two directions. On the contrary, F1-F4 compounds demonstrate the essential difference in this energy for zigzag and armchair directions. This difference is the largest for F2 and F4. For F1, F2 and F4 molecules the interaction energy along the armchair direction is larger than that for the zigzag one while for F3 molecule the opposite situation is observed.

To understand better the contribution of each ring of heterocyclic compounds to the total interaction energy of F1-F4 molecules and tetracene with graphene calculations of the hybrids formed by benzene and imidazole molecules with graphene were performed. Several locations of these small molecules on graphene were found and analyzed. In addition, the effects of CH3 and CF3 side groups attached to imidazophenazine on its arrangement on graphene and on the interaction energy between components were investigated.

DNA microcrystals on graphene surfaces: second harmonics generation

Galina Dovbeshko[1], Denys Pidhirnyi[1], Andrej Dementjev[2]

[1]*Institute of Physics, National Academy of Sciences of Ukraine, 46 Nauki Ave, Kyiv 03680, Ukraine*
[2]*Institute of Physics, Center for Physical Sciences and Technology, A. Goštauto 11, Vilnius LT-01108, Lithuania.*

The effect of the second harmonic generation (SHG) is well known for certain types of crystals. However this effect is studied insufficiently for the crystals of biological molecules. Earlier V. Gorelik [1] discovered SHG in the crystals of aminoacids. Here we present the data of SHG during CARS experiment with thymine crystals grown on glass and graphene surfaces. It is shown that adenine crystals, in contrast, do not give SHG under the same condition.

The picosecond laser (1,064 mkm) was used for the pump Stokes and excitation beams in CARS experiments, tuning range was the 690-900 nm. Such mixing of the beams allows probing of vibration frequencies from 700 to 4,500 cm−1. Both Stokes and pump beams were collinearly combined and directed to an inverted microscope.

Thy and Ade are essential components of DNA molecule and belongs to pyrimidine and purine bases respectively. The molecules are nearly planar with (001) crystal plane collinear with long molecular axis which connects C2O8 … C5C9 bonds. The tilt angle of molecular plane was estimated to be about 5° with respect to (001) plane. The planes of neighboring molecules in a layer are inclined at 6.60° with each other. The average interplanar spacing between adjacent layers in the (010) plane is about 3.36 Å. Pairs of molecules are connected by the N-H…O-C hydrogen bonds and form infinite chains along b axis. The unit-cell containing four molecules is monoclinic with the space group P21. The molecule of Thy and Ade belongs to the Cs group of symmetry. Therefore, both IR and Raman vibrational modes are expected to be active. Thymine gives rise to 39 vibrational modes. Ade crystallizes in monoclinic space group P21/c with 8 molecules in the unit cell.

Currently it is not completely clear why Ade does not show SHG effect. It could be explained by different properties of SHG in both crystals, namely by the absence of synchronism condition in the case of Ade. Additional studies of this phenomenon are required.

Aknowledgement. This work is supported by the Faemcar FP7-PEOPLE-2012-IRSES Project.

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Carbon nanoparticles as fluorescent probes for apoptosis detection

Mariia Dekaliuk, Kyrylo Pyrshev, Alexander Demchenko

Palladin Institute of Biochemistry, Laboratory of Nanobiotechnology, Kiev 01030, Ukraine, E-mail: mariiadekaliuk@gmail.com

Recently discovered inorganic carbon nanoparticles ("C-dots") due to their excellent fluorescence characteristics (1-2) and biocompatibility (3) have got a lot of interest for their use in imaging and functional transformations in living cells. The focus of our research was to determine the possibility of using C-dots as the easily available probes for early detection of apoptotic (committed to programmed death) cells.

The carbon nanoparticles were prepared from alanine, citric acid, urea, etc by hydrothermal treatment at 180 ^{0}C. As the fluorescent materials, the obtained structures are brightly fluorescent in the visible region, soluble in various organic solvents, stable at different pH and are non-toxic for the cell cultures. The studies were performed with Vero and HeLa cell lines. Two groups of cell were provided: living (intact) and apoptotic (camptothecin-treated) cells. Both groups were incubated with C-dots for an hour and all the changes were analyzed with spectrofluorometry, flow cytometry and confocal microscopy. We show that apoptotic cells accumulate significantly larger number of these fluorescent nanoparticles than living cells. Flow cytometry analysis of apoptotic cells stained with them showed homogenous distribution with higher signal than was provided by intact cells. Also marked changes were observed in the fluorescent intensity of C-dots localized inside apoptotic cells – they are additionally accumulated in the area of plasma membrane, which was never observed in living cells. Such effect was reproducibly observed with the both cell lines, and different types of applied C-dots.

Thus, we suggest simple and efficient method of detecting apoptosis that may be requested in different biophysical and biomedical studies, particularly for testing inducing apoptosis anti-cancer drugs. Its main advantage is the use of fluorescent nanoparticles that are easily synthesized in one step from different inexpensive precursors and do not require further modifications.

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Efficient white OLED based on the orange and blue exciplex emission

I. Helzhynskyy[1], **M. Chapran**[1], **V. Cherpak**[1], **P. Stakhira**[1], **G. Barylo**[1], **Z. Hotra**[1,2]

[1]*Lviv Polytechnic National University, S. Bandera 12, 79013 Lviv, Ukraine*
E-mail: email.of.author stakhira@polynet.lviv.ua
[2]*Rzeszów University of Technology, W. Pola 2, Rzeszów 35-959, Poland.*

Fabrication of OLEDs with the extended emissive spectral region and the minimal number of the functional layers is based on the idea that the layers of organic semiconductors should be able to form the exciplexes at the interface [1,2].

Detailed electroluminescence investigations of the exciplex type white organic light emitting devices (OLEDs) based on 4,4,4″-tris[3-methylphenyl(phenyl)-aminotriphenylamine (m-MTDATA), 4,4′,4′′-tri(N-carbazolyl) triphenylamine (TCTA) as donor and 4,7-diphenyl-1,10-phenanthroline (Bphen) as acceptor are carried out.

It was shown that the electroluminescence spectra of the fabricated device are more extended comparing with the photoluminescence spectra of all component materials. The observed extension of the electroluminescence spectra can be assigned to the emission of the exciplex formed at the interface of the emissive layers. The CIE coordinates (0.33, 0.42) of fabricated OLEDS corresponding to the white color.

Acknowledgment: This research was also supported by the “AmbiPOD” project (PIRSES-GA-2013-612670).

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The approach for fabrication of single nanocrystal devices

D.A Grynko[1,2], D.A.Galaktionov[2], E.G. Borschagovsky[1,2]

[1] Institute of Semiconductors Physics, Natl. Acad. of Sci. of Ukraine. Prospect Nauki, 41, Kyiv-03028, Ukraine.

[2] Institute of High Technologies, Taras Shevchenko National University of Kyiv , Prospect Glushkova,4-g, Kiev-02033, Ukraine, E-mail: dgrynko@gmail.com

Control of CdS nanocrystals growth from gaze phase as an approach for single crystal nanodevices fabrication will be discussed. We proposed to use the features of the self-organization of nanometer-scale semiconductor single crystals in the growth process from gaze phase for the manufacture of nanoelectronic and nanophotonic devices. Making of two types of nanodevices analyzed: ordered nanocrystal tripods and tetrapods as nanooptics components and field-effect resistor based on single nanocrystal grown in the interelectrode space.

The peculiarity of tripode and tetrapode nanocrystal element is the fact that under certain conditions its geometry is determined by the crystallographic structure of semiconductor substrates what governs the orientation of tripods, and only length is defined by the technological parameters of growth kinetics. Application areas of tripode and tetrapode nanocrystal are:

nanoantennas - detectors of infrared radiation;

electroluminescent devices with enhanced conversion efficiency due to nanoplasmonics;

biosensors;

converter of infrared laser radiation of 1.2 - 1.6 mkm into the visible optical range

Application of single nanocrystal element is biosensor which consists of microelectrodes and a one-dimensional single semiconductive nano- crystal connected in the electric circuit. Crystal surface modified with molecular monolayer capable of selective interactions with certain biological agents: proteins, RNA, viruses, etc. The principle of the simplest biosensor based on one-dimensional conductor is that the selective adsorption of a charged bio-agent leads to dramatic changes in electro conductivity.

Growth of semiconductor nanocrystals in the microelectrodes space is a self-organizing process suitable for one dimensional devices manufacture as opposed to existing technique of single crystal attaching to microelectrodes by micromanipulator and connecting into electric circuit by electron-beam lithography. Our approach to this problem is based on the use of processes of self-organization of semiconductor nanocrystals, which will allow us to grow nanocrystals with a given morphology, crystallinity, type of lattice and to form the complete device.

Carbon nanotubes and graphene in catalysis

R. Klimkiewicz [1], E. Kovalska [2],
O. Feniuk [3], V. Boiko [3], G. Dovbeshko [3], Yu.Sementsov [2]

[1]*Institute of Low Temperature and Structure Research PAS, 2 Okolna 2 street, Wroclaw, Poland*
[2]*Chuiko O.O. Institute of Surface Chemistry of National Academy of Sciences of Ukraine, 17 General Naumov street Kyiv, Ukraine*
[3]*Institute of Physics of National Academy of Sciences of Ukraine, 46, Prospect Nauki,46, Kyiv,03680, Ukraine*

High specific surface area, adsorption properties, resistance to acid/basic media makes carbon nanotubes (CNT) as well graphite, an extremely attractive material for heterogeneous catalysts. CNT can serve as a support for a catalytic surface phase that often consists of metal oxide clusters on the surface. In some cases they may reveal their own catalytic properties.

Different CNTs and graphene sheets directly influence on methane and phenol decomposition, oxidation of *p*-toluidine [1]. Catalysts based on CNT are more effective than traditional carbonaceous materials (graphite, activated carbon) [2].

Although, promising applications of such catalysts are transformations of oxygenates, one of them is the ketonization of primary alcohols in gas phase over heterogeneous catalysts. This process can be described by general equation:

$$2RCH_2OH \rightarrow 2RCHO \rightarrow RCOOCH_2R \rightarrow RCOR$$

Here we compare catalytic activity of graphene and CNT and got promising results .

Acknowledgment: we thank for financial assistance Ukrainian-Polish Joint Research Project (2015-2017).

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Synthesis, properties and application of graphene materials derived from multi-walled carbon nanotubes.

M.O. Danilov [1], I.A. Slobodyanyuk[1], I.A. Rusetskii [1], G.I. Dovbeshko [2], G.Ya. Kolbasov[1]

[1]*Vernadskii Institute of General & Inorganic Chemistry of Nat. Acad. Sci. Ukraine, prospekt Palladina 32-34, 03680 Kyiv 142, Ukraine.*
E-mail: danilovmickle@rambler.ru
[2]*Institute of Physics, Nat. Acad. Sci. Ukraine, prospekt Nauki 46, 03039, Kyiv, Ukraine.*

With the advent of new nanocarbon material - graphene, a number of papers were appeared on his research as an electrode material for lithium-ion batteries, sensors, and also as a carrier for the catalysts in fuel cell electrodes. Currently the following methods are known for synthesis the graphene from carbon multiwall nanotubes: intercalation; plasma etching; microwave unfolding; unfolding catalytic metal nanoparticles; ultrasonic unfolding; exposure to laser radiation; electric current; high-temperature hydrogenation; the impact of a scanning tunneling microscope; electrochemical unfolding; redox chemical synthesis. For studies we chose chemical synthesis. The chemical synthesis of graphene consist of the step of obtaining graphene oxide (GO) and its subsequent reduction to give the so-called the reduced graphene oxide (RGO).

Therefore, of great interest is the synthesis and study the properties of RGO and GO used as a catalyst for the oxygen fuel cell electrode. By the chemical synthesis we obtained the reduced graphene oxide from multiwalled carbon nanotubes. Applying a suitable oxidant may be longitudinally "expand" the nanotubes to form nanoribbons of graphene oxide, and then acting reducing agent to obtain the reduced graphene oxide. For selection of oxidant and reductant were used standard redox potentials of carboxy groups [1]. By various physical - chemical methods were shown that by the synthesis were obtained RGO and GO. From these materials were fabricated oxygen electrodes that have been investigated in the model of an alkaline fuel cell.

It was shown that this materials are stable and catalytically active catalyst carriers for the oxygen electrode, and not inferior in its electrochemical characteristics of catalysts based on noble metals.

1. *Danilov, M.O., Slobodyanyuk, I.A., Rusetskii, I.A., Dovbeshko, G.I., Kolbasov, G.A.* Influence of the Synthesis Conditions of Reduced Graphene Oxide on the Electrochemical Characteristics of the Oxygen Electrode // Nanoscience and Nanotechnology Research – 2014 - **2**, N 1 – P. 12-17

Three-dimensional structure from graphene nanoplatelets

[1]Sementsov Yu[2], Dovbeshko G, [1]Mahno S, [1]Aleksyeyeva T,[2] Styopkin V.

[1]*Chuiko Institute of Surface Chemistry, NASU, 17, General Naumov str, Kiev 03164, Ukraine,* ysementsov@ukr.net
[2] *Institute of physics NAS of Ukraine, Nauky Ave 46, 03028, Kiev, Ukraine*

On the most used method of graphene nanoplatelets production is dispersion of components, containing graphene monolayers obtained from natural graphite, artificial highly oriented pyrolytic graphite, expanded graphite (EG) intercalation compounds of graphite, oxide and fluoride of graphite, carbon nanotubes. The main advantages of this approach are perspectives of large scale production and relatively simple modification of graphene properties [1].

EG is a nanoscale clusters system comprising a cylindrical, conical or slit-like structures of 0.7-20 nm. The domain size of 20 nm was detected by X-rays coherent dispersion in tangent and normal direction [2]. Therefore, the EG is the most attractive precursor for graphene nanoplatelets for industrial production. Electrochemical intercalation (or anodic oxidation) is the most power saving method for obtaining EG in controlled conditions [3]. It allows achieving specified characteristics of the EG including adjusting the structural and chemical state of the surface. Repeated intercalantion of the material from the EG allows to reveal the nanoscale defects in the EG structure and to obtain the graphene nanoplatelets in aqueous electrolyte solution.

Graphene nanoparticles were obtained by repeated intercalation of graphite foil (TU 26.8-30969031-002-2002) under low concentration of alkaline electrolyte solution (KOH) and the electrical current in the range of 6.0- 60.0 mA/cm^2. The graphite foil served as an electrode. The nanoparticles were analysed by Raman scattering (RS) methods, laser correlation spectroscopy (LCS) and scanning electron spectroscopy (SEM).

The LCS analysis of the particles showed two fractions of particles in solution. The large particles (13 µm) sedimented after some time. The second group of the particles in the 20-450 nm range was more stable in solution. RS studies showed that characteristic peaks of the samples are similar to those of few graphene layers and graphite crystals (Fig.1).

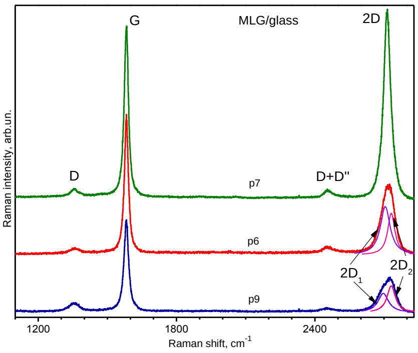
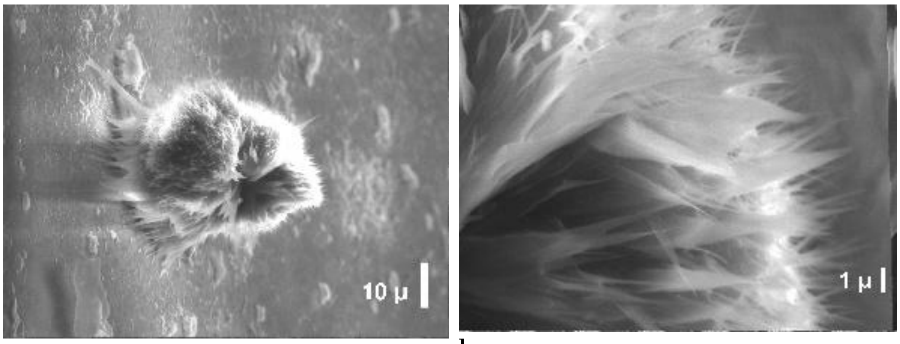


Fig.1. Raman spectra of the material generated during electrochemical processing of the foil EG.



a b

Fig. 2. The image of graphene particles with SEM (a, b,).

The solution after electrochemical treatment of graphite foil and separation from large particles was deposited on gold film substrate, dried and then analysed by SEM (Fig.2). Fig.2 clearly shows the lamellar structure of the particles. There are particles looking like "hedgehogs" formed from thin graphene plateletes with one end fixed at the same point. These "hedgehogs" are similar to the honeycomb surface of **EG** with significantly smaller cell size and thinner walls. Obtained results could be used in biomedical applications.

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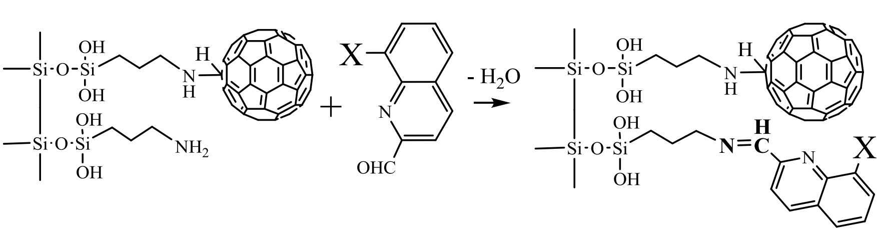
Catalytic Activity of Metal Complexes Immobilized at “Fullerene-Silica” Nanocomposite

O.L. Schur[1], E.O. Radchenko[1], A.A.Golub[1,2]

[1]Taras Shevchenko National University of Kyiv. 64 Volodymyrska str., Kyiv,01601, Ukraine, e-mail:nano.ukraine@gmail.com
[2]National University of Kyiv-Mohyla academy. 2 Skovorody str., Kyiv-04655, Ukraine, e-mail:agolub@univ.kiev.ua

Fumed silica with about 10 nm particle diameter and surface area of 290 m^2/g were used. The nanosilica surface was modified with propylamine groups ($[NH_2]$ = 0.89 mmole/g), and C_{60} fullerene by reaction with aminogroups in toluene media at the surface was immobilized and “fullerene-silica” nanocomposite (FSNC) so formed ($[C_{60}]$=0.15 mmole/g). 8-substituted quinoline derivatives at aminosilica and at FSNC were immobilized (Fig.). Cu^{2+}, Co^{2+} and Zn^{2+} complexes with immobilized ligands were synthesized from nonaqueous solutions.

UV-vis, IR and ESR spectroscopy data give possibility to propose the pseudo tetrahedral conformation for complexes at both surfaces at FSNC and at aminosilica without fullerene, so immobilized fullerene does not affect complex formation. The catalytic activity of nanocomposites in the hydrogen peroxide decomposition reaction was studied. It is noticed that only Co^{2+} complexes are catalytically active in the reaction. Furthermore, in the presence of fullerene at the surface the catalytic activity of the Co^{2+} complexes is more stable in time, but without fullerene the catalytic activity decrease after 200 sec of the experiment.



L1:X=OH(0.46 mmol/g); L2:X=OCOPh(0.55 mmol/g); L3:X=OCOtBu(0.49mmol/g)

Fig. Ligand immobilization reactions on fullerene-silica nanocomposite

Thus, C_{60} fullerene can stabilize catalytic activity of Co^{2+} complex in hydrogen peroxide decomposition reaction.

Schiff bases complexes immobilized at nanosilica as catalysts in ozone decomposition

T.L. Rakytska [1], A.S. Truba [1], E.O. Radchenko [2], A.A. Golub [2,3]

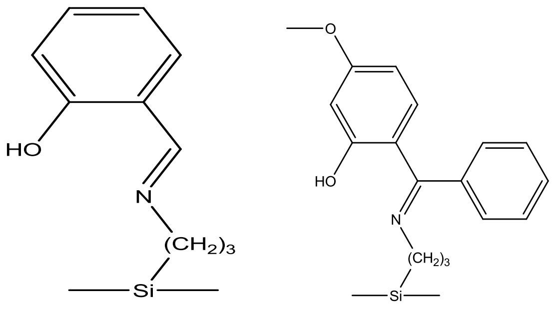
[1]Odesa I.I. Mechnikov National University, 2 Dvoryanska str., Odesa, 65082,
Ukraine, tlr@onu.edu.ua
[2]Kyiv Taras Shevchenko National University, 64 Volodymyrska str.,
Kyiv, 01601, Ukraine
[3]National University of Kyiv-Mohyla academy, 2 Skovorody str., Kyiv 04655,
Ukraine, agolub@ukma.kiev.ua

The influence of Mn(II), Co(II), Cu(II), Zn(II) and ligands, L1 and L2 (Fig) on nanocatalysts catalytic activity in ozone decomposition reaction were studied. The immobilization of a ligand and a complex formation were proved by IR and UV-VIS spectroscopy. When the complex is formed it shifts $\nu_{C=N}$ band in IR spectra to shorter wavelengths. The shift of $\nu_{\pi-\pi^*}$ band in UV-VIS spectra is also an evidence for a metal coordination. The half time of ozone decomposition (the bigger the better) is an evaluation parameter of complex activity. The influence of a central atom on catalytic activity of a mono complex could be represented as follows:

$Mn(L1)_2 > Co(L1)_2 > Cu(L1)_2 > Zn(L1)_2 > L1$ (I);

$Mn(L2)_2 > Co(L2)_2 > L2 > Cu(L_2)_2 \approx Zn(L2)_2$ (II).

The complexes with L1 are more active than complexes with L2. In addition, catalytic activity of immobilized ligand is different for L1 (I) and L2 (II). Bimetal complexes [Mn-M'-L1] and [Mn-M'-L2] (M' – Co, Cu, Zn) were synthesized by cooperative adsorption of two metals in equal concentrations. The catalytic activity of bimetal complexes could be represented as follows: $Mn(L1)_2$ > [Mn-Co-L1] > [Mn-Cu-L1] > [Mn-Zn-L1] (III) [Mn-Cu-L2] > [Mn-Co-L2] > [Mn-Zn-L2] > $Mn(L2)_2$ (IV)



L1 L2

Fig. Ligands L1 and L2 immobilized on nanosilica surface

The dependence of catalytic activity for L1, line I and III, is the same for mono- and bimetal complexes. The less an activity is of the second metal, the lower activity is of the bimetal complex. In case of L_2 the second metal M' = Cu(II), Co(II), Zn(II) increase catalytic effect of Mn(II) and besides in backward line II sequence. The close relations could be expected for bioactivity of complexes.

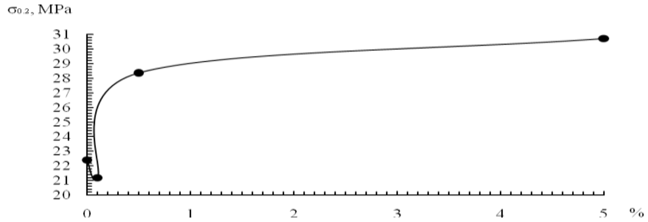
Mechanical properties of nanocomposites based multiwall carbon nanotubes and automated system of anisotropy analysis

<u>A.P. Onanko</u> , M.P. Kulish , G.T. Prodayvoda , Y.A. Onanko

Taras Shevchenko Kyiv national university, Volodymyrs'ka str., 64, Kiev-01601, Ukraine.
E-mail: onanko@univ.kiev.ua

The absolute value of the elastic module E, elasticity limit σ_E, inelasticity limit $\sigma_{0.2}$, ultimate stress limit σ_S of the nanocomposites based on multiwall carbon nanotubes (MWCNT) 5% + polypropylene, MWCNT 0,5% + polypropylene, MWCNT 0,1% + polypropylene were determined.

As aromatic groups, which are in different families of free monomers, are the effective traps of radicals, it allows to carry out their co-operating with MWCNT. Such co-operation due to covalently forces of connection results to fixing of polymeric chains nanotubes and also migrations of radicals on traps [1]. The concentration dependence of inelasticity limit $\sigma_{0.2}$ of nanocomposite based on MWCNT and polypropylene is represented on figure.



At the irradiation of composites with the increase of irradiation dose and concentration of nanotubes there are processes of sewing together of macromolecules which improve the specimen structure, that at lesser doses is accompanied the origin of nanostrains σi. With growth of absorption dose, at which the number of carbon internal atoms C_j is increased, both mechanisms of appearance of additional connections are assist in the improvement of hard properties, which is accompanied the growth of elastic module E, microhardness $H \approx \frac{E}{10}$ of nanocomposites at the increase of irradiation dose D.

Thus, the increase of nanocomposite crystalline degree at growth of MWCNT concentration, filling with the nanotubes of matrix results in the decline of content of well-organized phase.

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On the He-He bond paradigm in C_{60}-nanoconfinement

T.Yu. Nikolaienko [1], E.S. Kryachko [2]

[1] *Faculty of Physics, Taras Shevchenko National University of Kiev, Kiev-01601 Ukraine.*
E-mail: tim_mail@ukr.net

[2] *BogolyubovInstitute for Theoretical Physics, Kiev-03680 Ukraine.*
E-mail: eugene.kryachko@ulg.ac.be

The word ‘science’ originated from the Latin ‘scientia’ meaning a ‘knowledge’. That is, science aims to create a new knowledge – a set of the Truths – on the nature, or the world that daily surrounds us.

In 350 B.C., Aristotle began his famous book “Metaphysics” with the words:

“All men by nature desire to know”

which are applicable to all scientists, and to V. Kharkyanen in particular. The key motif of plethora of his works was the entire biomolecular world under which vault lies the concept of a chemical bond. The latter has been dramatically changed in nano-dimensions.

Perhaps a more notable example is the bonding patterns in He_2. Since 1928 when J. Slater made the first calculation of the bonding energy ΔE in He_2, only lazy physicists or quantum chemists have not calculated it. Actually, as a simple example: the MP2/cc-pV5Z computational level [1] demonstrates that the unique source of ΔE comes from the zero-point energy, thus reaching the value of 3.8 K at the He-He distance of ca. 3 Å [2]. This rather small energy is definitely insufficient to even sustain a single energy level to obey the necessary condition of the existence of a stable molecule, according to Löwdin (see e.g. [3]). During the last 15 years it was not clear whether the stable He dimer does exist [4].

However, the 1994th diffraction experiments provided the unequivocal evidence that $^4He_2$ does exists and is definitely a stable diatomic characterized by the averaged bond length of 52 Å and ΔE = 1.3 mK [4]. Another surprise for He_2 arrived in 2009 when Peng and Wang et al. [5] developed the explosion-based method and prepared the endohedral fullerene $He_2@C_{60}$, which existence was confirmed in their mass spectrum experiments.

Altogether, these led to a vague impasse: on the one hand, a void diameter of C_{60} comprises of 0.7 nm. On the other, in contrast, this void is thus insufficient to accommodate He_2 dimer since this void diameter is smaller the aforementioned mean He-He internuclear distance (e. g., 0.7 nm vs. 5.2 nm), and thus, rules out that He_2 dimer is still bonded in C_{60}, as was claimed in [5] that the He-He bonding in $He_2@C_{60}$ arises due to the following mechanism: the repulsive interaction between two helium atoms keeps them away from the center, thus approaching each to C_{60} surface and establishing a charge transfer between He and C_{60}.

To decipher this impasse on the He-He bonding in C_{60}, we propound a computational model that also includes smaller fullerenes, C_{20} and C_{28}, to demonstrate that encapsulation of He inside the studied fullerenes exhibits an interesting quantum behavior: all atoms belonging to the fullerene’s surface of a monoatomic thickness fractionally ionize He atoms that enables them to dimerize into a $He_2^{\delta+}$ dimer ($\delta > 0$). We interpret its He-He bonding pattern in terms of Bader’s ‘Atom-in-Molecule’ (AIM) theory. We conjecture a computational existence of $He_2@C_{60}$ on a solid basis of its theoretical UV absorption spectrum and a comparison with that of C_{60}.

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Nanostructured tunable mesoporous carbon for energy and biomedical applications

O. Gogotsi[1], B. Dyatkin[2], Y. Gogotsi[2], P. Simon[3], Y. Zozulya[1], B. Malinovskiy[1], V. Zahorodna[1]

[1] *Materials Research Centre, 3, Akademika Krzhyzhanovskoho St, Kyiv 03680, Ukraine, E-mail: E-mail: agogotsi@mrc.org.ua*

[2]*A. J. Drexel Nanomaterials Institute, and Department of Materials Science and Engineering, Drexel University, Philadelphia, PA 19104, USA, E-mail: gogotsi@drexel.edu*

[3] *Université Paul Sabatier-Toulouse III, CIRIMAT UMR-CNRS 5085, and RS2E, FR CNRS 3459, 118 Route de Narbonne, 31062 Toulouse, France. E-mail: simon@chimie.ups-tlse.fr*

Abstract

We will discuss synthesis of carbide-derived carbon (CDC), which is a nanoporous carbon formed by selectively etching metal atoms from metal carbides [1]. CDCs are generally produced by chlorination of carbides in the 200–1200°C temperature range. Metals and metalloids are removed as chlorides, leaving behind a noncrystalline carbon with up to 80% open pore volume. A wide range of carbide precursors (TiC, SiC, B_4C, VC, Mo_2C, NbC as well as ternary carbides – Ti_3AlC_2, Ti_2AlC, also known as MAX-phases) leads to a wide range of carbons with tailored porosity. The total volume and characteristic dimensions of meso- and nanopores can be predicted and achieved by selection of a binary or ternary carbide and variation of the chlorination process parameters. Due to a wide range of pore sizes (0.3–30 nm) and specific surface areas (300–2300 m^2/g) of CDCs, a great potential for applications requiring large volumes of either micropores (<2 nm) or mesopores (2–50 nm) has been identified [1].

The highly tunable porosity of CDC [1,2] has inspired fundamental studies of the effects of pore size, pore volume, and surface area on transport and adsorption of gases, ions and biomolecules. The unique properties of CDC allowed to use it in many demanding applications including H_2 and methane storage, gas sorption, adsorbents, electrodes in batteries and supercapacitors [3], flow capacitors, molecular sieves, catalyst supports, water/air filters and medical devices, protein adsorption, tribology, extracorporeal devices for blood cleansing [4]. Such properties of CDC as good electrical conductivity combined with high surface area, large micropore volume, and pore size control allow its application as active material in electrodes for flow desalination [5], supercapacitors [6] as porous electrodes for capacitive deionization [7] .

Chlorination of layered ternary MAX-phase carbides has made it possible to synthesize mesoporous carbons with large volumes of slit-shaped mesopores that can be used for purification of bio-fluids due to their excellent biocompatibility and ability to adsorb a range of inflammatory cytokines within the shortest time, which is crucial in sepsis treatment. The synthesized carbons, having tunable pore size with a large volume of slit-shaped mesopores, outperformed other materials in terms of efficiency of TNF-α removal. Cytokine removal from blood may help to bring under control the unregulated pro- and anti-inflammatory processes driving sepsis. Adsorption can remove toxins without introducing other substances into the blood. Therefore, hemoadsorption might have advantages over hemofiltration, having the same or better efficiency in the treatment of inflammatory diseases, being of lower cost and offering considerably better comfort for patients during and after the treatments [8]. Large mesopores in CDC from MAX phases are capable to accommodate most of the proteins due to their controlled porosity can be used for separation of different proteins molecules.

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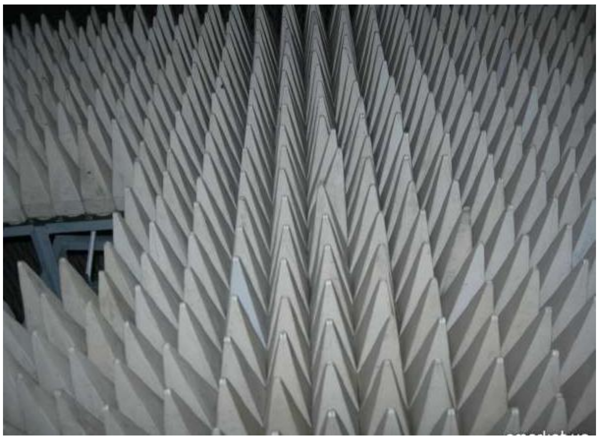
We offer the delivery of radar absorbing materials for the specified frequency ranges:

1 GHz – 18 GHz



The price of this material will be 285 dollar per 1 sq. m

Dielectric radar absorbing material pyramidal type in the form of panels for covering the internal surfaces and equipment jobs anechoic chambers.

Main features : Panel dimensions, mm from\to 250×250 to 1200×2400. Fire resistant polymer of the pyramid with the filling. The block size 83 x 83 mm x 250 (height) Unit weight, kg: 0,086. Weight of 1 m^2, 10 kg Item color Light grey. Operating temperature range, °C - 40.... + 60. The polarization - has a polarization properties. Toxicity Non-Toxic. Range, GHz 1 to 17

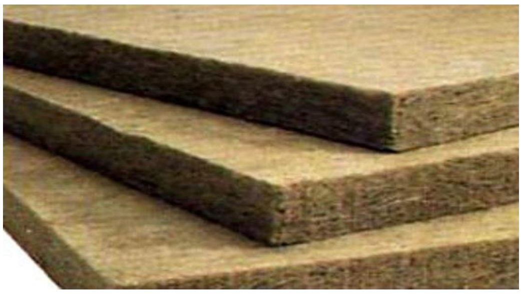
On the Frequency of GHz 0.5 1 2 4 10 20 the reflection coefficient (-dB), not exceeding 25 35 40 45 45 45

2. Range 80 – 1000MHz

The material is a two-layer flexible woven radar absorbing materials.

Specifications: The working wavelength range of 0.2-25 cm The reflection coefficient is not worse – 17 dB Weight of 1 m^2, kg 1,0 Operating temperature range + 60 C - 60 C Absorbing materials - environmentally safe self-extinguishing, resistant to moisture and lubricants. Scope: For equipment anechoic chambers

To eliminate unwanted electromagnetic background Ensuring environmental electromagnetic safety of biological objects, as well as addressing issues of passive protection against unauthorized access to information via radio channels. Advantages: Ultra-wide working range of wavelengths Easy mounting on stationary objects



The material cost for 1 sq. m. at a thickness of 110 mm to as high as 284 dollar.

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Contacts:

Prof. Galina Dovbeshko, +38(044)525-98-51, gd@iop.kiev.ua (experiments)

Dr. Semen Yesylevskyy, +38(044)525-79-91, yesint4@gmail.com (computations and theory)