National Academy of Sciences of Ukraine
Institute of Physics, Kyiv, Ukraine

March 1-2, 2022
Postponed September 9-10, 2022

Book of abstracts
International workshop

PHOTON – GRAPHENE INTERACTIONS: PHENOMENA AND APPLICATIONS-2

Organizers:

- **Institute of Physics, National Academy of Sciences of Ukraine, Kyiv, Ukraine**
- **Institute of Low Temperature and Structure Research, Polish Academy of Sciences, Wroclaw, Poland**

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ІНСТИТУТ ФІЗИКИ
Національна академія наук України

Kyiv, 2022

UDC 53.09

It was approved for publication by the Scientific Council of the Institute of Physics of NAS of Ukraine, Protocol № 5 on 25 August 2022

Book of abstracts of the International workshop "Photon – graphene interactions: phenomena and applications-2"
(March 1-2, 2022, Postponed September -9-10, 2022). – K.: Institute of Physics of NAS of Ukraine, 2022. – 56 p.

Book of abstracts contains reports presented at the International workshop. It is a meeting of scientists from Ukraine and Poland, who are at the forefront of theoretical and experimental studies of different phenomena including graphene lighting, hot electrons generation under lasers for electronics, photocatalysis etc. The program includes oral presentations led by eminent scientists and roundtable discussions. It will be the meeting place for new interdisciplinary scientific collaborations and networking. The goal of the conference is to discuss recent achievements and to push forward this innovative area of science and technology.

УДК 53.09

Затверджено публікації Вченою радою Інституту фізики НАН України, протокол № 5 від 25 серпня 2022

Матеріали міжнародного семінару «Взаємодія графен-фотон: ефекти та застосування»
(1-2 березня 2022 р., перенесено на 9-10 вересня 2022). – К.: Інститут фізики НАН України, 2022. – 56 с.

В збірнику представлені тези доповідей Міжнародного семінару. Це зустріч провідних вчених з України та Польщі, що займаються різносторонніми дослідженнями графену, зокрема свічення графену, генерації гарячих електронів під впливом лазерів для електроніки. фотокаталізу. тощо. Програма включає усні презентації, постерні доповіді та обговорення за тематичними круглими столами. Це буде місце зустрічі для нових міждисциплінарних наукових співпраць та контактів. Мета конференції - обговорити останні досягнення та просунути цю інноваційну область науки та техніки в Україні та Польщі.

УДК 53.09

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International workshop
Photon – graphene interactions: phenomena and applications-2

Conference hall of the Institute of Low Temperature and Structure Research, PAS, Wroclaw, ul. Okolna, 2 and Teams platform

Friday, 9 September, 2022		
Chairman – Leonid Yatsenko, Andrzej Jeżowski		
W 14:30-14:35 **K 15:30-15:35**	Opening the workshop	
W 14:35-15:05 **K 15:35-16:05**	**Wieslaw Stręk**	Memory effects in laser induced white emission of graphene and diamond
W 15:05-15:35 **K 16:05-16:35**	**Valeriy Gusinin**	Van Hove singularities and orbital susceptibility in Dirac materials
W 15:35-16:05 **K 16:35-17:05**	**Sergei Sharapov**	Optical and magneto-optical properties of monolayer graphene
16:05-16:35 Coffee Break		
Chairman – Leonid Yatsenko, Andrzej Jeżowski		
W 16:35-16:55 **K 17:35-17:55**	**Daria Szewczyk**	Heat capacity studies of carbon – carbon based low-dimensional composites
W 16:55-17:25 **K 17:55-18:25**	**Zdenek Sofer**	Chemistry of layered materials graphene and beyond
W 17:25-17:55 **K 18:25-18:55**	**Alexander Krivchikov**	About low-temperature heat capacity anomaly of strong anisotropic solids: nanostructured graphite oxide
W 17:55-18:15 **K 18:55-19:15**	**Serhii Kukhtaruk**	Collapse of plasmon-optical phonon branch in system of graphene on a polar substrate

W 18:15-18:35 **K 19:15-19:35**	**Andrey Solovjov**	"Effect of electron irradiation on fluctuation conductivity and pseudogap in $YBa_2Cu_3O_7$-δ twin single crystals
W 18:35-18:50 **K 19:35-19:50**	**Vitaliy Boiko**	White-light emission from 2D MoS_2 and WS_2 powders
Saturday 10 September 2022		
Chairman – Wieslaw Stręk, Galyna Dovbeshko		
W 10:40-11:00 **K 11:40-12:00**	**Maxim Barabashko**	Thermal stability of thermally reduced graphene oxide
W 11:00-11:15 **K 12:00-12:15**	**Mykhailo Chaika**	White-light emission generation from graphene-based microchip
W 11:15 11:35 **K 12:15 -12:35**	**Przemyslaw Wiewiorski**	High-intensity strobe light source based on simultaneous electro-optical effects on 3D porous graphene
W 11:35 -11:50 **K 12:35 -12:50**	**Vardan Apinyan**	Optical property of the half-filled bilayer graphene
W 11:50-12:10 **K 12:50-13:10**	**Włodzimierz Mista**	Efficient Generation of Hydrogen by Laser Irradiation of Graphene Porous Particles in Ethanol
W 12:10 -12:30 **K 13:10-13:30**	**Galyna Dovbeshko**	Coherent anti-stokes Raman scattering spectroscopy (CARS) and imaging of graphene and DNA on graphene layers
W 12:30 -13:00 **K 13:30-14:00**	Chairmans – Leonid Yatsenko, Wieslaw Stręk, Sergey Sharapov, Ivan Blonsky, Valeriy Gusynin, Andrzej Jeżowski	
Round Table "Graphene for lighting"		
Concluding remarks		

Van Hove singularities and orbital susceptibility in Dirac materials.

Valerij Gusynin

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Square-octagon lattice underlies the description of a family of two-dimensional materials such as tetragraphene. We show that the tight-binding model of square-octagon lattice contains both conventional and high-order van Hove points. In particular, the spectrum of the model contains flat lines along some directions composed of high-order saddle points. Their role is analyzed by calculating the orbital susceptibility of electrons. We find that the presence of van Hove singularities (VHS) of different kinds in the density of states leads to strong responses: paramagnetic for ordinary singularities and more complicated for high-order singularities. It is shown that at doping level of high-order VHS the orbital susceptibility as a function of hoppings ratio α reveals the dia- to paramagnetic phase transition at some point. This is due to the competition of paramagnetic contribution of high-order VHS and diamagnetic contribution of Dirac cones. The results for the tight-binding model are compared with the low-energy effective pseudospin-1 model near the three band touching point.

White-light emission generation from graphene-based microchip

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Since its discovery in 2010 by Tanner and Wang, the Laser Induced White Emission (LIWE) has attached a lot of attention in the last decade [1]. The main feature of LIWE is a broadband emission, which covers the entire visible and part of the NIR regions, like solar radiation. This makes it possible to create new white light sources with a high color rendering index of the emitted light.

The aim of this work was to study LIWE phenomenon at λ_{exc} = 975 nm from a graphene microchip. The graphene foam synthesis was carried out by the sol-gel method with graphene oxide used as a precursor. The graphene-based microchip was fabricated based on a quartz vacuum chamber and graphene foam 0.2 mm thick superimposed on the inner wall (Fig. 1(a)). The emission spectra were measured on an AVS-USB2000 spectrometer.

The interaction of laser beam at the power above the threshold leads to the appearance of strong emission in the visible and NIR region (Fig. 1(b)). It was found that an intense white lighting occurs simultaneously from the front and back surfaces. The number of photon (N) involved in LIWE process is 6 (Fig. 1(c)). LIWE process was accompanied by a strong photoelectric effect, with the photoconductance yield increasing exponentially with the applied laser power of similar order as the power dependence of the LIWE intensity. The observation of the white emission has been discussed in terms of a gap opening due to the light induced $sp^2 \rightarrow sp^3$ transition [2].

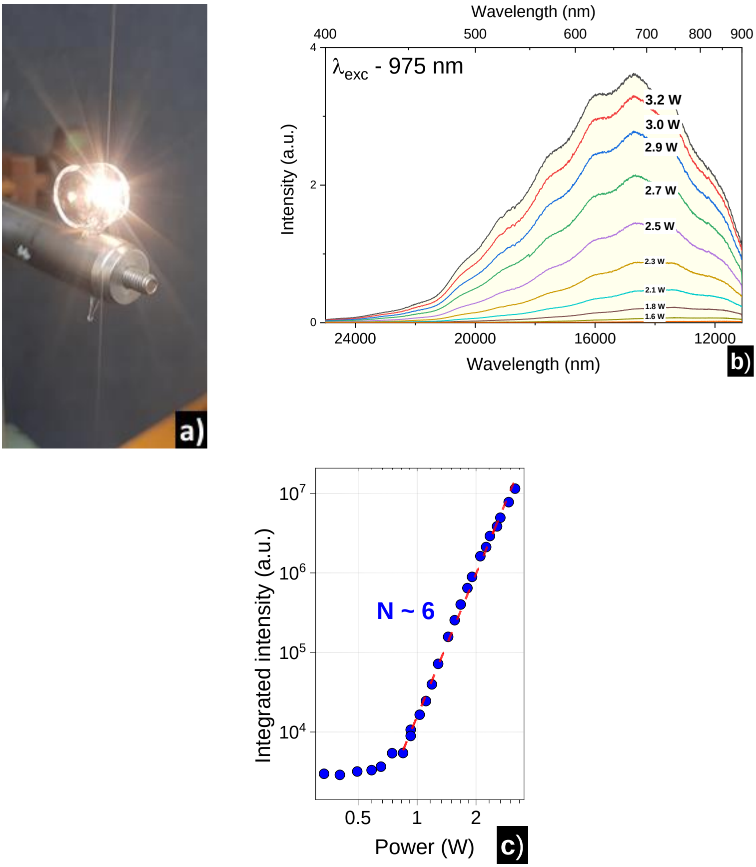

Fig. 1: a) Photo of the graphene microchip.
b) Emission spectra from graphene microchip and
c) power dependence of LIWE measured at λ_{exc}-975 nm in vacuum.

1. J. Wang, P.A. Tanner, *Journal of the American Chemical Society*, 132(3), 947-949 (2010).
2. W. Strek, R. Tomala, M. Lukaszewicz, et. all, *Scientific Reports*, 7(1), 1-9 (2017).

Could the negative capacitance effect be used in FETs with a ferroelectric gate?

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We consider a silicon MOSFET, in which the gate insulator is formed from thin layers of a dielectric SiO_2 and a weak ferroelectric, such as HfO_2, or graphene-like low-dimensional transition metal dichalcogenides. We study the possibility of implementing a stable negative capacitance of the insulator in such a system, which would open the principal possibility to reduce the subthreshold swing to the values below the threshold, 60 mV/decade at room temperature, and supply voltage to the values below the fundamental Boltzmann limit, 0.5 V, which would be an important step towards further miniaturization of MOSFETs. It is shown theoretically that it is possible to achieve a transient negative capacitance of a ferroelectric in the situation when the charge at the capacitor plates increases more slowly than the ferroelectric polarization. Note that the negative capacity is fundamentally transient. Its temporal stabilization in thin dielectric and ferroelectric layers requires stable positive free energy and capacity of the whole system. Therefore, the effect of the negative capacitance of a ferroelectric itself cannot be manifested "outside" the ferroelectric, including the transistor applications and it is unrealistic to hope that the negative capacitance effect will help reduce the subthreshold swing below the critical value, and thus contribute to further miniaturization of the MOSFET.

Size Effect of Local Current-Voltage Characteristics of Graphene-Like Low Dimensional Dichalcogenides

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Local current-voltage characteristics for graphene-like low-dimensional transition metal dichalcogenides (LD-TMD), as well as the reconstruction of their local density of states (LDOS) from scanning tunneling microscopy (STM) experiments is of fundamental interest and can be useful for advanced applications. Using a serial expansion of Tersoff formulae, we propose a flexible method how to reconstruct the LDOS from local current-voltage characteristics measured in STM experiments. We established a set of key physical parameters, which characterize the tunneling current of a STM probe – sample contact and the sample LDOS expanded in Gaussian functions. Using a direct variational method coupled with a probabilistic analysis, we determine these parameters from the STM experiments for MoS_2 nanoflakes with different number of layers. The main result is the reconstruction of the LDOS in a relatively wide energy range around a Fermi level, which allows insight in the local band structure of LD-TMDs. The reconstructed LDOS reveals pronounced size effects for the single-layer, bi-layer and three-layer MoS_2 nanoflakes, which we relate with low dimensionality and strong bending/corrugation of the nanoflakes. We hope that the proposed elaboration of the Tersoff approach allowing LDOS reconstruction will be of urgent interest for quantitative description of STM experiments, as well as useful for the microscopic physical understanding of the surface, strain and bending contribution to LD-TMDs electronic properties.

Acknowledgments

This work (A.N.M., H.V.S., Y.Yu.L. and G.I.D.) has been supported by the National Research Fund of Ukraine (project “Low-dimensional graphene-like transition metal dichalcogenides with controllable polar and electronic properties for advanced nanoelectronics and biomedical applications”, grant application 2020.02/0027). Project “Development of 2D materials and “smart” sensors for medical and biological purposes” 11/1–2022.

Thermal stability of thermally reduced graphene oxide

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Thermal stability of the thermally reduced graphene oxide (TRGO) has been studied. Modified Hummers method was used for obtaining the initial graphite oxide (GO) from graphite powder. The thermal exfoliation of the graphene oxide powder has been performed in the vacuum conditions at 300°C. For partial graphene hydrogenation, TRGO has been treated by pulsed high-frequency discharge in a hydrogen atmosphere that leads to structural changes in the carbon planes and the formation of C-H sp^3 bonds. The TGA measurements of the mass loss have been carried in a nitrogen atmosphere from room to 1000°C. Kissinger's multiple heating rate method has been used to determine the activation energy for decomposing substances. Obtained activation energies have been compared with the energies of the activation of thermal defunctionalization of multi-walled carbon nanotubes (MWCNTs). Obtained experimental results are useful for further proposing the kinetic model of the mechanism of the most probable reaction of TRGO decomposition.

Acknowledgments
We appreciate National Research Foundation of Ukraine (Grant No.197/02.2020) for support of our investigations.

White-light emission from 2-D MoS_2 and WS_2 powders

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The LIWE (Laser Induced White-Light Emission) phenomena has received much attention in recent years. LIWE has been detected in a vacuum and is characterized by broadband emission covering the entire Vis and NIR regions. Several possible mechanisms of LIWE have been proposed, however, the mechanism behind this phenomenon is still not entirely clear. The aim of this work was to investigate LIWE phenomena at λ_{exc}-975 nm from 2-D graphene-like materials [1]. For this, WS_2 and MoS_2 commercial nanopowders (Aldrich) were used. Emission spectra were measured using two types of detectors: AVS-USB2000 and NIRQuest512-2.5.

The interaction of a laser beam at the power above threshold (around 1 W) leads to the appearance of strong emission in the Vis and NIR region (Fig. 1). LIWE spectra of MoS2 are characterized by a higher emission intensity in the 700-900 nm regions in contrast to WS2. The number of photons (N) involved in LIWE process was 5 for both materials at low pump power, while N dropped to 3 at higher pump power for WS2. The difference in behaviour may be related to the structure and optical property of these materials and requires further investigation [2].

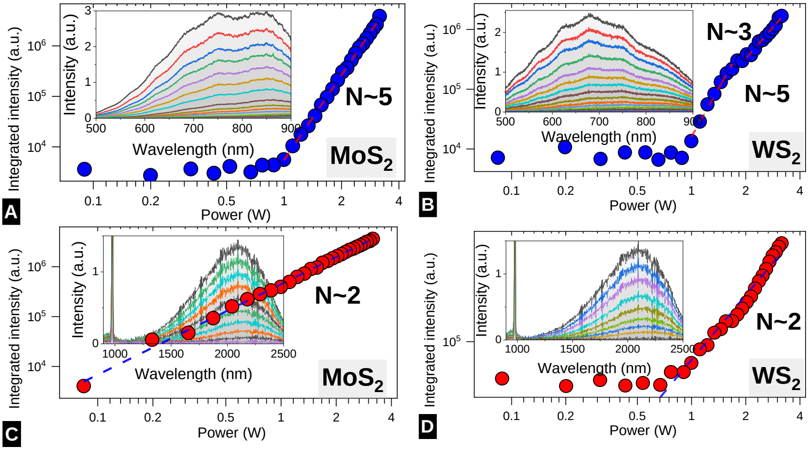

Fig. 1: The power dependence of LIWE from MoS_2 (a, c) and WS_2 (b, d) detected in the Vis (a, b) and NIR (c, d).

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2. Strek, W., Cichy, B., Radosinski, et. all, *Light: Sci. & Appl.*, **4**(1) (2015), e237-e237.

Collapse of plasmon-optical phonon branch in system of graphene on a polar substrate

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We show that the dispersion equation approach can give the ambiguous solutions, if the dispersion equation contains the branch points. In particular, in the case of strong coupling between plasmons of graphene and surface optical phonons of a polar substrate, the solutions of the dispersion equation depend on branch cuts. This issue can be solved, if one consider initial value problem instead of the standard dispersion equation approach. In this case, we show that the plasmon-phonon mode, which in terms of the dispersion can have a good quality factor, almost absent in the spectrum, i.e., this mode collapses. Evidences of the collapse can be seen in already published relevant experiments with this system. We present detailed analysis of plasmon-phonon modes in the system - graphene-polar substrate. We suggest that these results can be important for applications of graphene based plasmonics.

Efficient Generation of Hydrogen by Laser Irradiation of Graphene Porous Particles in Ethanol

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Hydrogen energetics is a center of massive investigations in last year due to civilization challenge for application of clean energy fossil fuels. Mass production of hydrogen is proceeded commonly by electrolysis, thermolysis and photolysis of hydrocarbons. The efficient generation of hydrogen in suspension of graphene foam particles in ethanol was proceeded by irradiation with CW infrared laser diode operating and 980 nm. It was observed a cyclic response of emission of different gases - H2, CO, CH4 resulting from laser induced ionization of graphene and fragmentation reactions of ethanol. The hydrogen generation increased linearly with excitation laser power. Mechanism of the process was discussed. The main products of laser induced dissociation of ethanol apart of H2 were CO and CH4 .

It was observed that the production volume of hydrogen increases linearly in time and this increase is strongly dependent on excitation power. The time dependence of generation of hydrogen volume VH produced at different excitation power is plotted in Fig. 1a. One can see that the volume of hydrogen increases exponentially with applied laser power. The total flow of H2, CO and CH4 gases was determined to be 156 ml/h. In this amount the total flow of H2 was estimated to be 73 ml/h =3.2 mmol/h for the highest power of applied IR laser 4 W, as depicted in Fig. 1b.

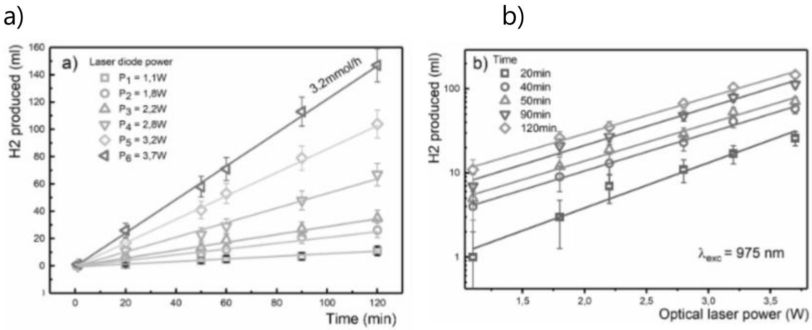

Fig. 1. Evolution of generated H2 volume from ethanol +GP solution irradiated with CW 980 nm laser diode in time for different excitation power (a). The power dependence of H2 volume generated from (ethanol +GP) irradiated with CW 980 nm laser diode in different time intervals (b).

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2. 2 W. Strek, P. Wiewiórski, W. Miśta, R. Tomala, M. Stefanski, Laser-Induced Generation of Hydrogen in Water by Using Graphene Target, Molecules, 2022, 27(3), 718.

Memory effects in laser induced white emission of graphene and diamond

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Laser induced white emission of graphene diamond single crystal in vacuum bulb was investigated under irradiation with CW 1064 nm laser diode. The measurements of power dependence of emission intensity were performed under the forward (increasing) and backward (decreasing) excitation conditions demonstrating a hysteresis loop. The loop area has been diminishing significantly with decreasing excitation power. It is concluded that the hysteresis indicates an appearance of optical memory that is discussed in terms of forming a stable reservoir of (sp^2,sp^3) hybrid pairs due to multiphoton ionization.

About low-temperature heat capacity anomaly of strong anisotropic solids: nanostructured graphite oxide

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The low-temperature thermal properties of highly anisotropic solids differ significantly from those of conventional crystals and glasses. In my report, it will be shown that this is mainly due to the appearance of anomalous dispersion of one of the acoustic branches in the dispersion law of a strongly anisotropic solid. Using the low-temperature heat capacity of nanostructured graphene oxide as an example, the reasons that lead to the suppression of both the calorimetric Boson peak and the van Hove singularity in the vibrational density of states are explained.

Acknowledgements

This work was supported by National Research Foundation of Ukraine (Grant № 2020.02/0094)

Laser Femtosecond Complex within the Institute of Physics of NAS of Ukraine: facilities and applications

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The Laser Femtosecond Complex within the Institute of Physics of NAS of Ukraine was put into operation in 2005, aiming initiation and development in Ukraine of the investigations of ultra-fast electronic processes at femto- picosecond time scale, laser-induced structural transformations in materials under intense optical excitation of up to 1 EW/cm^2, precise laser technologies of micro-processing of materials, and for education and training of graduate and PhD students in the field of laser physics at the state-of-the-art level.

The following experimental techniques have been developed:

- "pump-probe" for transient absorption measurements (temporal resolution is 150 fs, spectral range is 450÷650 nm;
- "Kerr gate" for secondary emission measurements (temporal resolution is 300 fs within 2 ns time domain, spectral range is 350÷1050 nm);
- "Z-scan" for nonlinear optical characterizations;
- laser pulse compression up to 65 fs;
- femtosecond time-resolved polarization microscopy technique for direct observation of space-time transformations of a femtosecond laser pulse in transparent media (temporal resolution is 65 fs, spatial resolution is 2 μm);
- microscopy technique of femtosecond time-resolved shadowgraphy (temporal resolution is 65 fs, spatial resolution is 2 μm).

The following fundamental studies have been performed:

- filamentation of laser radiation;
- induced anisotropy of surface plasmons;

- conical light emission;
- sub- and superluminal light pulse propagation;
- supercontinuum white-light emission within 300 nm ÷ 4 μm spectral range;
- laser-induced periodic surface structure formation.

Examples of practical applications:

- arrays of microlenses and micromirrors have been produced;
- biocompatibility of implants has been improved by laser-induced surface structuring;
- kinetics of laser damage of materials has been studied in femto-nanosecond time domain;
- optical recording and erasing has been demonstrated in copper-silica nanocomposite.

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Magnetoconcentration effects in intrinsic graphene ribbons

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We consider transverse redistributions of the electrons and holes in intrinsic graphene ribbons under the influence of crossed electric and magnetic fields, i.e., the magnetoconcentration effect. The electron and hole transport is described from the Boltzmann kinetic equation assuming the local quasiequilibrium distributions of the carriers over energy states. The effective control of the carriers is achieved from deep depletion to accumulation modes depending on the properties of the ribbon edges, provided electron-hole recombination/generation rates at the edges are different from those inside the ribbon. The current-voltage characteristics reflect the behavior of the carrier redistributions across the ribbon.

The obtained results suggest that interesting effects such as the population inversion in certain ranges of energies and the induced transparency are possible, which make them attractive for various optoelectronics applications in the terahertz spectral range.

Raman characterization of Graphene nanoparticles infiltrated into the synthetic opal pores

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The presence of a periodic structure in photonic crystal (PC) leads to observations of the photonic stop bands due to light scattering on the periodically located scatters and electric field localization in the cavities of the PC (hot spots formation). The distribution of the local electric field can be controlled by the geometrical and optical parameters of the PC structure as reported from FDTD calculations in [1].

Graphene nanoparticles (GNP) 0.7-1.8 nm (2-5 graphene layers) in thickness and about 20-50 nm in length fabricated by mechanochemical delamination [2] were deposited from water-ethanol colloidal solution on the surface as well in the pores of PC based on synthetic opal. Our estimations from AFM measurements gave that about 7% of silica globules surface area of the near-surface layers of PC are covered with 2D graphene NPs. This amount of globule surface coverage by GNPs, in terms of volume fraction, corresponds to 0.5-1.5% of the volume of the cavities.

For PC with such small amount of GNP materials in cavities we have observed a suppression of opal crystal luminescence intensity resulting in clearing of Raman spectra of materials investigated. This can be the basis for creating a combined substrate for surface-enhanced spectroscopy of bio-macromolecules.

Mapping of PC surface infiltrated with GNP performed for D, G and 2D mode have shown that GNP infiltrated into opal pores reveal lower defect grade than GNP on the surface of Si. This may be due to the fact that size of the GNP aggregates placed at the surface of flat Si substrate is bigger than size of GNP infiltrated between opal domains.

Our experimental data are in agreement with the simulation of local electromagnetic field distribution by FDTD methods. When excitation occurs with energy match the photonic stop zone, light penetrates to a depth of about 10 monolayers of globules, and when excited outside the stop zone - much deeper. At the same time the so-called "hot spots" with high electric field intensity are formed, although in the second case the field intensity is lower. It seems that in such a system it is possible to achieve greater improvement by adjusting the size of the globules to build a PC and using the graphene nanoparticles as inclusions.

Acknowledgements

This work has been supported by the National Research Fund of Ukraine (project “Low-dimensional graphene-like transition metal dichalcogenides with controllable polar and electronic properties for advanced nanoelectronics and biomedical applications”, grant application 2020.02/0027) and project “Development of 2D materials and “smart” sensors for medical and biological purposes” 11/1–2022.

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Optical and magneto-optical properties of monolayer graphene

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The experimental investigation of the optical and magneto-optical properties of graphene played a substantial role in the verification of the Dirac nature of charge carriers in graphene. We overview main properties of graphene such as universal optical conductivity and behavior of the absorption lines in the magneto-optical conductivity that are caused by the Dirac-like character of the low-energy quasipartcle excitations in graphene. In a weak magnetic field the ac conductivity oscillates around the universal value and the Drude peak evolves to the peak at the cyclotron frequency. The optical conductivity sum rules are presented.

Structural transformations of graphene oxide during reduction and modification

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Graphite oxide, formerly called graphite acid, is a compound of carbon, oxygen and hydrogen in variable ratios, which is obtained by treating graphite with strong oxidants and acids [1]. The most oxidized bulk product is a yellow (yellow-white) solid with a C/O ratio between 2.1 and 2.9, which preserves the structure of the graphite layer, but with a much larger and irregular interplanar distance [2, 3]. Solid material spontaneously disperses in basic solutions or can be dispersed by ultrasound in polar solvents, forming monomolecular sheets known as graphene oxide (GO) by analogy with graphene, a single-layer form of graphite [4].

The aim of the current study was to establish changes in the structure and state of the surface of GO under the conditions of its reduction and modification by hetero atoms of nitrogen and amino acids. Reduction of GO was performed with hydrazine hydrate (R-GO), doping with nitrogen atoms - urea impregnation and subsequent heat treatment (N-GO), and the surface of GO was modified with sulphur-containing amino acid - L-cysteine by nucleophilic addition (L-GO). The obtained samples were characterized by analytical methods, such as Raman scattering, IR spectroscopy, TPD-mass-spectrometry, dynamic light scattering spectroscopy. The available Raman spectra indicate a defective structure of GO, reduction of GO leads to greater ordering of the structure in relation to GO, nitrating and modification by amino acid - to the opposite effect, a slight deterioration of the structural state (Fig. 1, Table 1).

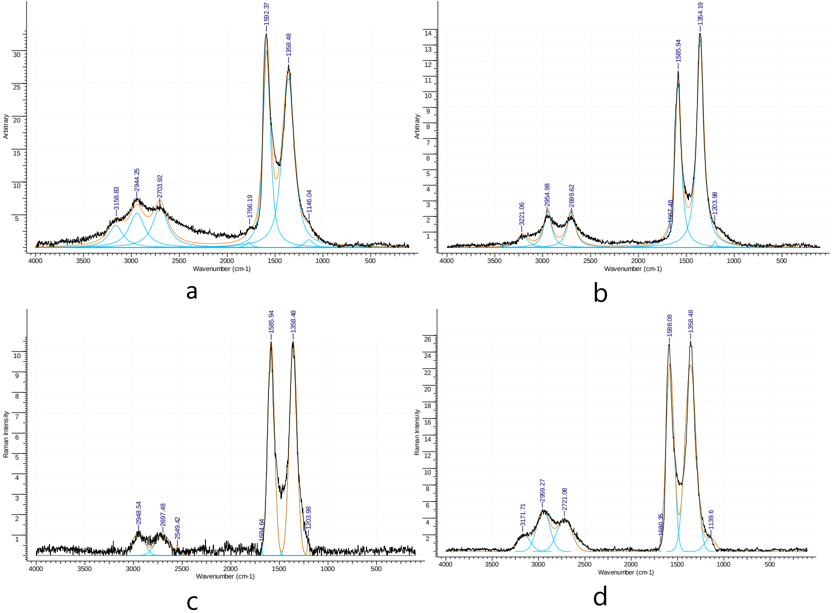

Fig. 1 – Spectra of Raman scattering and deconvolution of these spectra in the form of Gauss-Lorentz bands after manual subtraction of the baseline: a) - graphene oxide (source); b) reduced graphene oxide; c) - nitrided; d) - modified with L-cysteic acid.

The particle thickness of graphene La was calculated by the formula [5]: $L_a(nm) = (2.4 \times 10^{-10})\lambda_l^4 \left(\frac{I_D}{I_G}\right)^{-1}$, where: λ_l – is the wavelength of the excitation radiation (in our case it is 488 nm), ID is the intensity of the D-band, IG is the intensity of the G-band. The thickness of GO particles is 16 nm, and the number of layers - 15±1. Then for the reduced, nitrided and acid-modified GO the particle thicknesses will be 10.5 nm, 13.6 nm and 12.4 nm. Thus, the reduction of GO makes the particles thinner, obviously, this does not change the number of layers, but changes the distance between the layers.

Table 1

The values of some basic parameters of the characteristic bands manifested in the micro-cattle of GO samples and its restored and modified forms and their values (*) according to the results of deconvolution in the form of Gauss - Lorentz bands.

№ sample	**1**	**2**	**3**	**4**
Synthesis conditions	GO-initial	R-GO	N-GO	L-GO (cysteic acid)
Shooting conditions	λ=488 nm, P=1 mW, p3	λ=488 nm, P=1 mW, p1	λ=488 nm, P=1 mW, p2	λ=488 nm, P=1 mW, p1
D, cm^{-1}	1358,5	1354.0	1358,5	1358,5
D(-),cm^{-1}	1146.7	1204.0	1204,0	1140,0
G, cm^{-1}	1592.4	1586.0	1586.0	1581.3
G(+),cm^{-1}	1766.2	-	-	-
D_{FWHM}, cm^{-1}	172.3	109.6	137.7	139.8
G_{FWHM}, cm^{-1}	104.6	105.3	111.3	94.3
$2D_1$, cm^{-1}	2704.0	2700,0	2697,5	2721,0
$2D_2$, cm^{-1}	2944.5	2955.0	2948,45	2959.0
$2D_3$, cm^{-1}	3159.0	3221.0	-	3172,0
$2D_{1FWHM}$, cm^{-1}	406.6	227.9	279.5	278.8
$2D_{2FWHM}$, cm^{-1}	152.6	198.2	153.6	186.4
$2D_{3\ FWHM}$, cm^{-1}	181.4	126.3	-	157.4
I_D, relative unit	23.7	11.9	9.6	23.0
I_G, relative unit	29.0	9.2	9.5	20.3
I_D/I_G	0.82	1.3	1.0	1.1
I_{2D1}/I_G	0.12	0.14	0.1	0.17
I_{2D1}, relative unit	3.5	1.3	0.9	3.4
I_{2D2}, relative unit	3.0	1.4	0.8	4.1
I_{2D3}, relative unit	2.0	0.3	-	1.7

According to the results of IR spectroscopy, also confirmed by TPD-MS, GO has a large number of functional surface groups: (OH), (C=O), (C=C), (C-O-C), (CO-O-CO), (CH). Hydrazine reduction completely hydrophobicizes the surface, in the IR spectra there is only a peak at ~ 1040 cm^{-1}, which corresponds to CO-O-CO fluctuations, with significantly reduced intensity, as well as bands at 2120 cm^{-1} and 2300 cm^{-1}, which indicate about the aromatic nature of the samples and exist in all GO derivatives. In nitrogen and sulphur-containing samples (L-GO) a new peak of ~ 1520 cm^{-1} appears, which corresponds to N-H fluctuations in amines. Sulphur-containing derivatives have valence fluctuations at 600 cm^{-1}, which most likely corresponds to S-H bonds. Thus, modification of GO leads to a significant change in its structure and surface chemistry, which in turn affects the ability of the obtained samples to capture free radicals. Previous empirical studies have shown that this property increases in the series L-GO> GO> N-GO> R-GO.

Acknowledgments

The work was performed with the grant support of the National Research Fund of Ukraine project 2020.01 / 0107

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Quantum-chemical investigation of the superoxide radical scavenging activity of graphene oxide surface

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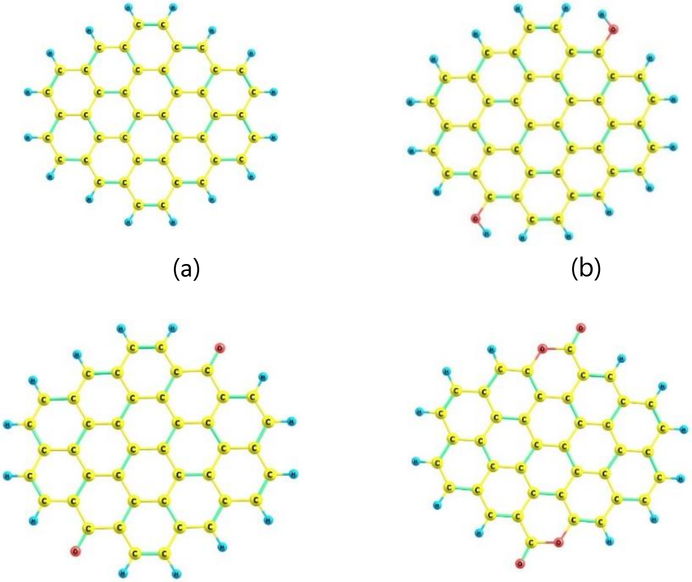
Carbon nanomaterials demonstrate free radical scavenging effect, that based on their possibilities to generate radical adducts at sp^2 carbon sites, to transfer surface electrons, to donate the hydrogen from functional group. Carbon-based materials showed significant activity against OH* radical, modest one against H_2O_2 and lipid peroxyl radicals, and stable radicals including DPPH and ABTS. Regarding this, graphene oxide (GrO) has a set of important features and a large surface area that takes an important role in its scavenging properties. Hence, the aim of this investigation was to study the mechanism of the interaction of superoxide radical with graphene surface.

Superoxide radical scavenging activity was evaluated using quantum-chemical calculations that were performed within the framework of the density functional theory (DFT) with the functional B3LYP and the basis set 6-31G (d,p) with Grimme-D3 corrections using the Firefly 8.2.0 program. A conjugated polyaromatic cluster $C_{42}H_{16}$ ($Gr|^{Clus}$) and clusters with different oxygen-containing groups (hydroxyl, ketone, and pyrone; $GrO|^{Clus}$) were used to simulate a graphene and graphene oxide respectively (Fig. 1). The size of selected clusters is much bigger than superoxide radical (SR, O_2^{*-}), therefore, any edge effects are negligible.



(a) (b)

(c) (d)

Figure 1. Polyaromatic clusters used in this work: (a) – initial $C_{42}H_{16}$ (Gr|^{Clus}); (b) – midified with two hydroxyl groups GrO|$^{Clus(OH)}$; (c) midified with two carbonyl groups GrO|$^{Clus(C=O)}$; (d) midified with two pyrone groups GrO|$^{Clus(O\text{-}C=O)}$.

Interaction of the SR radical with Gr|^{Clus} and GrO|^{Clus} in an aqueous environment was considered as a substitution of the water molecules to SR radical on the surface. Adsorption energies $\Delta E_{ph.ads}$ and $\Delta E_{chem.ads}$ were calculated using the following formulas:

$$\Delta \mathrm{E}ph.ads = \left((E_{tot}(2nH_2O) + E_{tot}(Gr|^{Clus} \ldots O_2^{*-})\right) - \left((E_{tot}(O_2^{*-} \ldots nH_2O) + E_{tot}(Gr|^{Clus} \ldots nH_2O)\right)$$

$$\Delta \mathrm{E}chem.ads = \left((E_{tot}(2nH_2O) + E_{tot}(Gr|^{Clus} - O_2^{*-})\right) - \left((E_{tot}(O_2^{*-} \ldots nH_2O) + E_{tot}(Gr|^{Clus} \ldots nH_2O)\right)$$

where E_{tot} ($2nH_2O$) – total energy of the cluster, consisting of 2n water molecules; E_{tot} (Gr|^{Clus} ···$O_2^{\bullet -}$) – total energy of the physical adsorption complex; E_{tot} (Gr|^{Clus}–$O_2^{\bullet -}$) – total energy of the chemical adsorption complex; E_{tot} ($O_2^{\bullet -}$···n H_2O) – intermolecular complex of the adsorbate molecule with a water cluster; E_{tot} (Gr|^{Clus}···n H_2O) – total energy of the hydrated surface of graphene plane.

We started from the modeling of the physiological environment (aqueous media). The water clusters (WClus) that have been chosen in the current study are presented in Fig. 2. It consists of five water molecules that are united in a five-membered ring (so-called homodrome cluster). After replacement of water molecules on the $Gr|^{Clus}$ by SR, WClus of 10 water molecules is formed (10-WClus). An energy diagram of the interaction of SR radical with hydrated $Gr|^{Clus}$ in aqueous media is presented in Fig. 2. The 5-WClus and $Gr|^{Clus}$ form an intermolecular complex connected via hydrogen bonds and oriented parallel at the distance of 2.5 – 3 Å (Fig. 2, left picture). Simultaneously, at the interaction of SR with 5-WClus, the structure of the last one is changing.

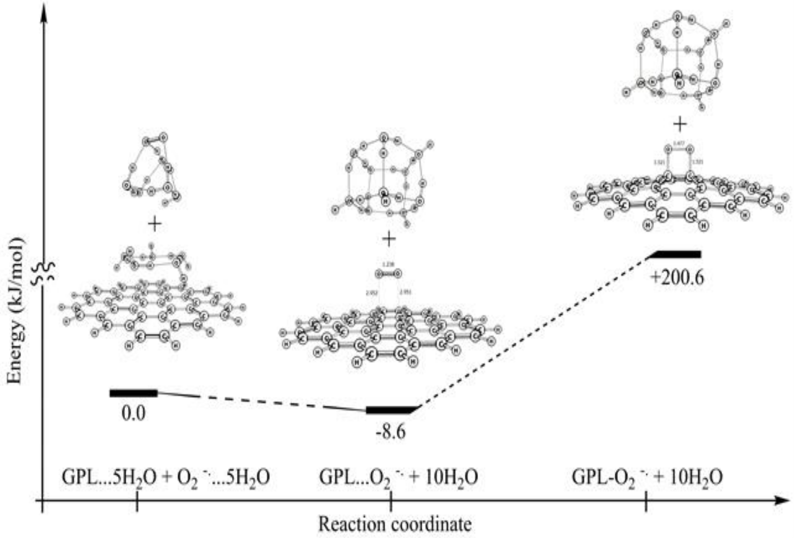


Figure 2. Energy diagram of the interaction of SR with hydrated $Gr|^{Clus}$ in aqueous media.

After replacement of the 5-WClus to SR, both 10-WClus and intermolecular complex are formed at a distance of 2.95 Å (Fig. 2, centered picture). This process is thermodynamically possible due to the energy effect ($\Delta E_{ph.ads}$) of it that is - 8.6 kJ/ mol. Further coming of SR to the $Gr|^{Clus}$ leads to the chemisorption complex occurring (Fig. 2, right picture), in which two covalent bonds are formed between carbon and oxygen atoms with a length of 1.52 Å. In this case, the O –

O distance in SR increases from 1.24 Å to 1.48 Å. It could be assumed that electron density from the SR redistributes to the $Gr|^{Clus}$. However, chemisorption energy ($\Delta E_{chem.ads}$ is + 200.6 kJ / mol) indicates the low probability of formation of this chemisorbed complex in an aqueous solution. The same calculations were done for $CrO|^{Clus}$ and obtained data are presented in Table 1.

Table 1.

Energy characteristics of the SR interaction with different graphene clusters

Graphene clusters	$\Delta E_{ph.ads}$, kJ / mol	$\Delta E_{chem.ads}$, kJ / mol
$Gr|^{Clus}$	-8.6	+200.6
$GrO|^{Clus(OH)}$	+32.1	+207.8
$GrO|^{Clus(C=O)}$	-109.7	+123.5
$GrO|^{Clus(O-C=O)}$	-10.7	+148.6

Thus, the analysis of the calculated results shows that the presence of different functional groups on the graphene plane significantly affects the energy effect of the chemisorption reaction and the redistribution of electron density in the formed complexes. Quantum chemical calculations indicate that the highest energy of physical sorption (- 109.7 kJ / mol) is for GrO surface with ketone groups on the periphery, whereas the lowest value (+ 32.0 kJ / mol) – for GrO with hydroxyl groups. The energy values of the chemical sorption in all cases are much higher than zero that indicates the unposibility of such interaction. Most likely SR scavenging effect on the graphene surface occurring via the physically sorbed state.

Acknowledgments

The work was performed with the grant support of the National Research Fund of Ukraine project 2020.01 / 0107

Chemistry of layered materials graphene and beyond

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Graphene is intensively explored in last decades. This unique material exhibit several possibilities for chemical modifications in order to control its physical and chemical properties. Introduction of various chemical functionalities will be discussed. Beyond graphene the other related materials remain almost unexplored. The research activities in the field of other layered materials like phosphorene, arsenene, silicene and germanene are rapidly growing in the last few years. Compare to graphene, all these materials are non-zero band-gap semiconductors. This property opens new application possibilities in electronic and optoelectronic devices. The properties of 2D materials can be further controlled by their functionalization. The chemistry of materials beyond graphene is none explored and shows high application potential in many fields. Compare to the graphene and pnictogen group, the chemical exfoliation method mast be applied for synthesis of silicene / germanene derivatives using Zintl phase compounds like CaGe2 and CaSi2. Various methods well know from organic chemistry can be applied for synthesis of tetrel derivatives reaching almost complete derivatization of 2D material skeleton.

Zdenek Sofer is a professor at the University of Chemistry and Technology Prague since 2019. He received his PhD also at University of Chemistry and Technology Prague, Czech Republic, in 2008. During his PhD he spent one year in Forschungszentrum Julich (Peter Grünberg Institute, Germany) and also one postdoctoral stay at University Duisburg-Essen, Germany. Research interests of prof. Sofer concerning on 2D based materials covering graphene, pnictogens, silicene, layered chalcogenides and other 2D nanomaterials, its chemical modifications and various applications covering electrocatalysis, gas separation and energy storage. Currently prof. Z. Sofer act as an associated editor of FlatChem Journal. He published over 460 articles, which received over 19 500 citations (h-index of 69).

Solution-processed graphene for flexible triboelectric nanogenerators

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A rapid development of wearable technologies for healthcare or security applications has raised demanding requirements for portable and sustainable power sources. A flexible triboelectric nanogenerators (TENG) are found to be an appropriate wearable approach to combine body motions with vital signs monitoring. However, this technology is high-costly and suffers from low power output and unstable electric output values. Herein, we demonstrate flexible TENG integrated with shear force exfoliated multilayer graphene (MG). The MG was exfoliated in an ethanol-water mixture and spray-coated on a nylon substrate. The ML on nylon served as an electrode material. Further MG was coated with beeswax that served as an active triboelectric layer. Triboelectric response of as-fabricated MG on nylon TENG (size 1.5x2.5 cm) was tested with a cyclic physical stimulus. The device showed open-circuit voltages of 25 V and short-circuit currents of 400 mA when stimulated at 1 Hz frequency. The output can be significantly higher (up to 5-10 times) when compared to devices with a size 3x3 cm. The power density output of 0.01 W/cm2 under a load of 62 kΩ was achieved, which is approximately 60 times over that of planar rigid graphene-based TENG. These results pave the way to the potential of solution-processed graphene for low-cost flexible triboelectric devices for harvesting ambient vibration energy.

Low frequency vibrational modes of 6-thiopurine in Ar matrices and composite films with graphene oxide: FTIR spectroscopy analysis and quantum mechanical calculations

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6-thiopurine (6TP), minor nucleobase with useful biological properties, has notable infrared spectrum in the low frequency spectral region of 900-200 cm-1, due to structural molecule features. In this region most of the absorption bands of 6TP can be attributed to non-planar modes [1]. We found that the calculated frequency of out-of-plane vibration γN7H (Q27) is in good agreement with the experimental spectrum (Fig. 1). In addition, several absorption bands are observed near the out-of-plane (Q29) ring mode. It was shown that in this spectral range, as for adenine [2], the Fermi resonance is realized with the involvement of librational modes. Note that the frequencies of librational vibrations of impurity molecules in inert matrices may be in the range 30–120 cm–1. Comparison of the experimental spectrum with the calculated one makes it possible to assign the absorption bands FR4 (565 cm-1) and FR5 (582 cm-1) to the combination bands enhanced by Fermi resonance (Fig. 1).

Another feature of 6TP spectrum is the vibration peculiarity of the pyrimidine and purine rings around the common bond C4C5 ("butterfly"): Q33, Q35 [1]. A high-frequency shift of these modes in matrices is observed in experimental and calculated spectra (Fig. 1). Calculations showed that the stacking energy of 6TP/GO complex is 3 kcal/mol higher than the base stacking energy in the dimer or trimer of 6TP. In the experimental spectra of composite film, it was revealed that the 6TP interaction with GO is accompanied with the frequency shift of low-frequency out-of-plane vibrations of 6TP molecules.

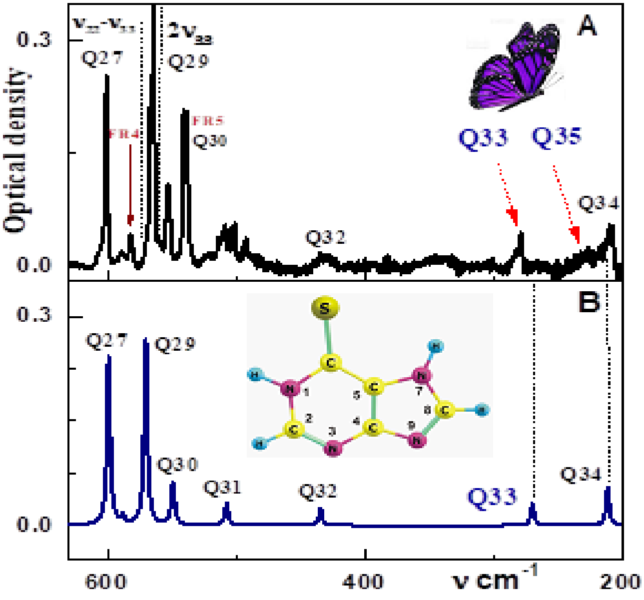

Fig. 1. (A) FTIR spectrum of 6TP in Ar matrix (T = 8K, M / S = 700). (B) calculated spectrum by the DFT/B3LYP/6-311++G(df,pd) method for the main tautomer of 6TP. FRi – combination mode changed by Fermi resonance. Dotted lines show the frequencies of possible combination bands.

Acknowledgments

We acknowledge financial support from National Academy of Sciences of Ukraine (Grant No. 0120U100157) and the authors thanks High Throughput Computing (HTC) at the University of Arizona for the computational resources.

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Optical property of the half-filled bilayer graphene

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We consider the optical properties of the half-filled AB-stacked bilayer graphene with the excitonic pairing and condensation between the layers. Both intra and interlayer local Coulomb interaction effects have been taken into account and the role of the exact Fermi energy has been discussed in details. We have calculated the absorption coefficient, refractive index, dielectric response functions and the electron energy loss spectrum for different interlayer Coulomb interaction regimes and for different temperatures. Considering the full four-band model for the interacting AB bilayer graphene, a good agreement is achieved with other theoretical and experimental works on the subject, in particular, limiting cases of the theory. The calculations, presented here, permit to estimate accurately the effects of excitonic pairing and condensation on the optical properties of the bilayer graphene. The modifications of the plasmon excitation spectrum are discussed in details for a very large interval of the interlayer interaction parameter.

Heat capacity studies of carbon – carbon based low-dimensional composites

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Development of a new graphite based material consisting from graphite nanoparticles (more 97 %) filed with multiwall carbon nanotubes (CNTs) (1-3%) entailed a much wider need in their properties determination. Generally, due to the unique structures and intimate interactions in-between, graphene-carbon nanotubes hybrids have significantly improved most of the properties, proving great potential for application in energy- and environment-related fields. In order to reach full utilization of the synergistic effect between exfoliated graphite and multiwalled carbon nanotube (EG-MWCNT) a new technological method was proposed, namely anodic oxidation of condensed expanded graphite.

In our studies, special focus was placed on thorough and detail characterization of interfacial phenomena observed in thermal transport studies of unique nanostructural carbon – carbon composites, where different effective density of the composite is varied by changing the filament – matrix ratio. The preliminary studies cover heat capacity investigations of composites prepared by different synthesis methods, which seems to have an impact on the resulting properties of the specimen, especially in low temperature regime. The importance of determination the main thermal transport mechanisms and the observed interfacial phenomena is as followed: in nanostructures, the interfaces are particularly important due to the decreased component size, which significantly increase the number of interfaces, and as a consequence affects many properties of the system, including thermal ones, crucial in micro/nanoelectronics applications.

Acknowledgments

Dr. O. Romantsova is thankful for a research grant founded under the agreement between the Polish Academy of Sciences and the American National Academy of Sciences.

CARS image Segmentation for sets of DNA and graphene-covered glass

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DNA was deposited on the monolayer graphene-covered glass substrate from the aqueous solution with concentration (1mg/ml). CARS images of DNA were registered using a home-built CARS microscope with a compact laser source (EKSPLA Ltd.). The pump and Stokes pulses of 6 ps at 1 MHz repetition frequency were provided by 1064 nm Nd:YVO4 laser and a travelling wave optical parametric oscillator (OPO) operating in the wavelength range from 690 to 2300 nm, respectively. For calculation of quantitative and qualitative parameters of DNA, first of all it is necessary to separate pixels of DNA image from those of monolayer graphene-covered glass. The CARS images consist of a resonance signal from DNA and a non-resonance one from the substrate.

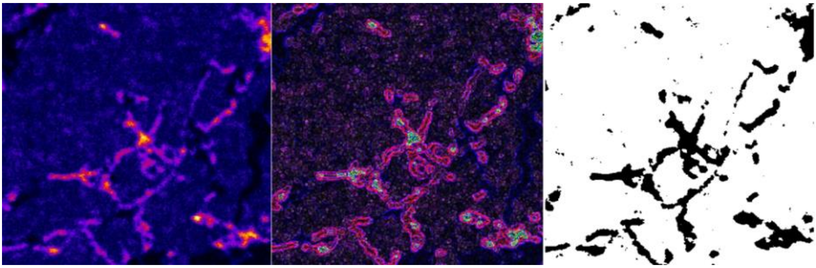

Fig. 1. (a) – original CARS image, (b) – Sobel-Feldman operator image processing, (c)– separated pixels of DNA on graphene-covered glass.

The method of image segmentation is based on the use of the Sobel-Feldman operator. At the first step, an array of pixels is separated that make (build) up the DNA structures. This array does not contain absolutely all the pixels comprising the DNA image, but every pixel from this set belongs to the DNA structure. At the second step, this set is processed and as a result, the global binarization threshold of the original image is calculated. At the third step, based on the calculated global binarization threshold, the entire image is divided into two sets, namely, the set A (pixels that make up DNA structure) and the set B (substrate pixels that are not a part of DNA structure).

The data from the RGB color model are converted to the HSL color model (hue, saturation, lightness (intensity)). Let a lightness L be a numerical representation of the light absorption intensity of DNA and the graphene substrate. Let's draw an L histogram for the both pixel sets and calculate a standard deviation of L arithmetic mean for the A (SA) and B (SB) pixels sets. These parameters represent fluctuations of L value for pixels from each of the sets - SA = 0.003716, SB = 0.001257. As a result, the L value fluctuations for the pixels from the set A are three times lower than those from the set B. This observation corresponds to the physical nature of CARS imaging DNA and underlying graphene substrate.

The pixels of the set A are clearly divided into three subsets with low, medium and high L value. Let subtract from the set A its intersection with the set B over the L value. As a result, the set A does completely lose its lower L value subset and includes only two subsets comprising the medium- and high-value L. The latter corresponds to Fig. 1b showing the application of the Sobel–Feldman operator to identification of two different sets of pixels in the CARS image of the DNA structures.

Fig. 2. demonstrates the partition of the set A by the maximum value LBmax of the set B into two subsets A1 and A2. A1 is a subset of pixels with L>LBmax and A2 is a subset of pixels with L< LBmax. The pixels of the subset A2 mainly lie at the boundaries between the substrate and the A1 subset pixels.

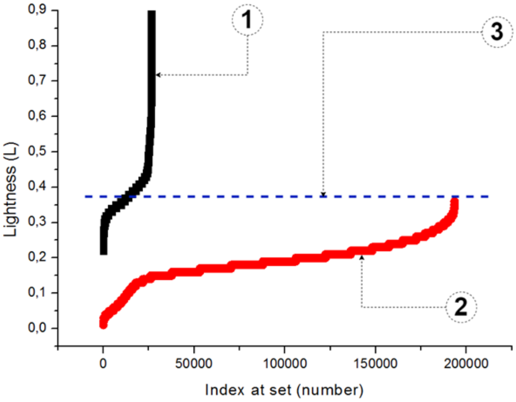

Fig. 2. Histogram of lightness L of pixels from original image: 1 – lightness LA of pixels from the set A (DNA), 2 – lightness LB of pixels from the set B (graphene-covered glass), 3 – threshold of intersection of LA and LB)

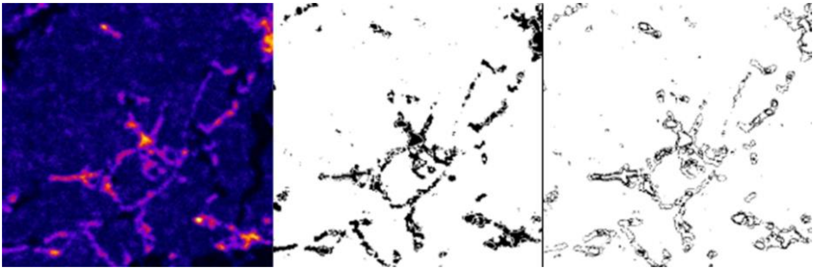

Fig. 3. a – original CARS image, b – subset A1 - non intersection of A set with B by L value , c – subset A2 - intersection of Set A with set B by L-value.

Therefore, the pixels of A2 subset are the regions of uncertainty where the original recorded analogous signal, after registration and digitization, could belong to both the DNA structure and the substrate. As a result, the A1 subset (Fig. 3b) is the required set of pixels, containing the data only from the DNA structures.

"Effect of electron irradiation on fluctuation conductivity and pseudogap in $YBa_2Cu_3O_7$-δ twin single crystals

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After more than 30 years since the discovery of high-temperature superconductors (HTSCs) the microscopic mechanism which provides the superconducting (SC) pairing above 100 K is still controversial. According to modern concepts, in order to understand the nature of the SC state and various unusual properties of HTSCs, one has to study the pseudogap (PG) state [1], which is observed below the PG opening temperature, T* >> Tc.

To shed more light on the nature of PG, the effect of electron irradiation (with the energy of 2.5 MeV) on the temperature dependences of the resistivity ρ(T) of the optimally doped $YBa_2Cu_3O_7$-δ twin single crystal has been studied. For the first time, the temperature dependences of both the fluctuation conductivity σ´(T) and PG Δ*(T) on the irradiation dose ϕ have been calculated from resistive measurements within the local pair model [2]. It has been convincingly shown that both σ´(T) and Δ*(T) exhibit very unusual behavior with a striking feature at ϕ3 = 4.3×1018 e/cm^2, which is also observed in the number of other dose dependent parameters [3]. At ϕ3 the shape of σ´(T) and Δ*(T) changes significantly and becomes the same as in optimally doped $YBa_2Cu_3O_7$-δ single crystals, with a very low T* and noticeably reduced pairing temperature Tpair, while at

$T_c(\phi)$ and $\rho(T, \phi)$ there are no singularities. With an increase in the irradiation dose up to $\phi 4 = 8.8 \times 1018$ e/cm^2, the shape of both σ´(T) and Δ*(T) is restored and becomes the same as in well-structured $YBa_2Cu_3O_7$-δ films and untwined single crystals.

Phoshorenes as a new class of materials for surface enhanced spectroscope application or not?

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Surface enhanced spectroscopy (SES, namely, SEIRA and SERS) effect is evident on different nanostructured metallic surfaces. Last time the authors have applied graphene and graphene-like MoS_2 and WS_2 supports for the signal enhancement however the results were not as good as for metallic surfaces. The electromagnetic mechanism of SERS according to [1], being a result of both charge transfer and dipole−dipole coupling, does not provide an enhancement coefficient of more than 100 for graphene or graphene oxide substrates in SERS and about 10 in SEIRA. In general, with application of 2D-graphene-like substrates as MoS_2 or WS_2 or even 2D-BN without special arrangement it is practically impossible to reach an enhancement by more than 10 in SERS and several units in SEIRA.

Phosphorene is a promising two-dimensional material consisting of phosphorus, namely, of a single layer of the artificially made layered black phosphorus, which is known as the most stable allotrope of phosphorus.

In contrast to graphene, phosphorenes have a non-zero fundamental band gap that can be further modulated by strain and the number of layers. They have strong in-plane anisotropy and high carrier mobility. That is why we can expect that the phosphorenes will show similar behaviors as graphene substrates and will be more preferable than MoS_2 or WS_2.

Here we present a SEIRA experiment on a model biological cell membrane on 2D-phosphorene surface that demonstrates up to 3-4 enhancement coefficient contrary to its 30% enhancement on WS_2. Thus, the data obtained by us with a model membrane on the phosphorene substrate are similar to that reported by the authors [2] for similar ATR experiment with biological cells localized on the surface of colloidal silver particles. That is why we can conclude about strong electromagnetic field caused by 2D-phosphores in the vicinity of very inhomogeneous surface of membrane. Taking into account that the optical signal from membrane is negligible, this technique could be recommended for application of 2D-phosphorene as a SEIRA and SERS substrate.

Ab-initio calculations of the systems thymine-graphene, thymine-WS_2, thymine-MoS_2, thymine-2D-phosphorene showed that charge transfer in the systems according Bader analysis 10^{-1}, 10^{-3}, 10^{-3}, 10^{-2} takes place. Thus, the amount of charge transferred for phosphorene is similar or slightly more than that for MoS_2, WS_2, and by an order less than for graphene. However the experiment with cell membrane indicated it's more strong electromagnetic interaction with 2D-phosphorous, the reason could be a transformation in the structure of interacting surfaces or arising local fields. That is why we can expect better SES effect for new 2D-phosphorous materials compared to that already registered for 2D-MoS_2 or 2D-WS_2, and, in special cases, even for graphene.

Acknowledgement

We acknowledge the Ukrainian-Czech joint project «Phosphorenes as novel promising material for biochemical application» 2022

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Coherent anti-stokes Raman scattering spectroscopy (CARS) and imaging of grapheme and DNA on graphene layers

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We report a comparative study of the Raman and Coherent anti-Stokes Raman scattering (CARS) patterns of DNA molecules deposited on graphene or glass substrates. In the DNA CARS spectra, the positions of vibrational resonances are red-shifted by 10–20 cm^{-1} and have new features in high-frequency region in comparison with spontaneous Raman data. We demonstrate that CARS imaging can be employed for the visualization and characterization of DNA molecules deposited on graphene. Peculiarity of CARS spectrum of graphene is discussed on the basis of Fano resonance model.

High-intensity strobe light source based on simultaneous electro-optical effects on 3D porous graphene

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In present work we demonstrate a new concept of efficient generation of high power white light source based on the flash electrical current flow through graphene scaffold. Synergy of electro-optical phenomena with assisted continuous wave laser diode irradiation of graphene was developed. It was observed that the strobe light occurred very intensively during current flow through the whole surface of 3D porous graphene affected by IR laser irradiation.

Graphene material has extremely low resistivity. Typical 10mm long 3D porous graphene has about 1 ohms that mean 2 range lower than graphite structures. It is possible to produce high impact-type electrical current flow through the graphene material higher than 10 kA/µs using dedicated power supplies.

At described experiment contact between electrodes and graphene was not stable so high current flow was appeared by single microsecond period range that induced high-intensity light. After some cooling time of the bulb next shot was possible.

The light induction on whole 3D graphene surface is very rapid effect similar to arc xenon bulb.

Future application includes the possibility to build high power UV-rich light source based on graphene so called arc tubes with spectra characteristic modified by synergy of electric and magnetic field during current flow and laser irradiation.

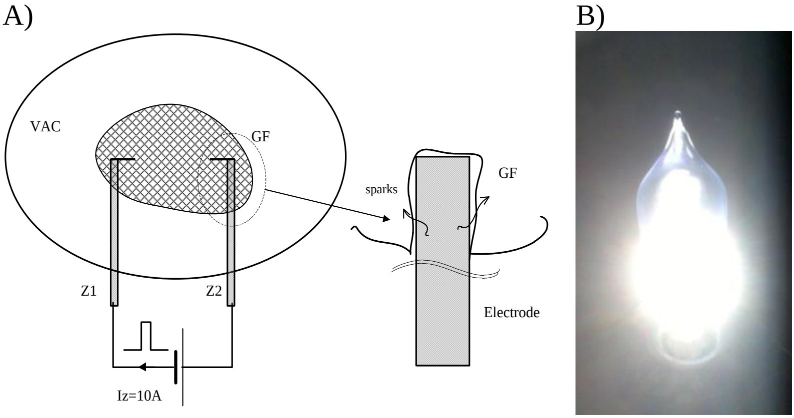

Fig. 1. Scheme of setup for powering flash graphene bulb with unstable contacts A), photo of strobe light effect on 3D porous graphene

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Наукове видання

Взаємодія графен-фотон: ефекти та застосування

Тези доповідей міжнародного семінару
Інститут фізики НАН України,
м. Київ, Україна та м. Вроцлав, Польща, 9-10 вересня, 2022

Підп. до друку 30.08.2022. Формат 60x84/16
Папір офсетний. Друк цифровий. Зам. №33/11-1
Ум. друк. арк. 2,75. Обл.-вид. арк. 1,35. Наклад 20 прим.

Видання здійснено в авторській редакції.
Надруковано з оригіналів автора.
Відповідальні за видання:
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