Form 21

APPROVED

JINR Vice-Director

“_____” _____20 г.

SCIENTIFIC-TECHNICAL VALIDATION ON THE OPENING OF THEME FOR INCLUSION IN THE 2018—2020 JINR TOPICAL PLAN

Theme code:
04-4-11…-2018/2020

Frank Laboratory of Neutron Physics
Sector of Raman Spectroscopy

Field of research: 04 – Condensed Matter Physics; Radiation and Radiobiological Research

Theme title: “Modern Trends and Developments in Raman Microspectroscopy and Photoluminescence for Condensed Matter Studies”

Theme leaders: G.M. Arzumanyan, N. Kučerka

Abstract

The activities implemented in the framework of the previous theme # 04-4-1111-2013/2017 demonstrated the relevance of this topic and, not least, the stable operation of the multimodal optical platform based on the microspectrometer “CARS”. It should be noted that conducted in 2015-2016 upgraded programme of the optical platform has made it possible to bring this tool to the number of modern and unique Raman microspectrometers, which have no analogues in terms of their functional characteristics and capabilities in Russia and in the CIS countries today. The "CARS" microspectrometer is also quite competitive at the world level in its class of analytical instruments.

The above mentioned items formed the basis for the proposal to open a new theme aimed at developing and realizing modern methods of ultrasensitive, selective detection of single/unit molecules using nonlinear modalities of Raman scattering. First of all, we consider spectroscopy of coherent anti-Stokes Raman scattering (CARS) of organic molecules localized on nanostructured surfaces that provide surface-enhanced Raman scattering by these molecules using ultrashort (picosecond) laser pulses. This phenomenon is known as the Surface-Enhanced Coherent anti-Stokes Raman Scattering - SECARS. Note that around the world in this area published by now only about 20 original works.

The first stage experiments for the implementation of this complex and ultrasensitive technique were successfully carried out in 2017 in the Sector of Raman Spectroscopy, FLNP. However, for its full-scale, stable and reproducible implementation, it is necessary to conduct complex experimental and technical work. Special attention will also be paid to the theoretical

support of experimental studies, including modeling of nonlinear processes of interaction of picosecond pulses with molecules adsorbed on nanostructured substrates.

Another modern component of the theme is the study of photo- and upconversion luminescence based on promising "core-shell" nanostructures. In the recent years core-shell nanoparticles are at the leading edge of the hot research topics and offer a wide range of applications in optics, biomedicine, environmental science, materials, energy, and so forth, due to their excellent properties such as versatility, tunability, and stability.

After studying the spectral and structural characteristics of such luminescent phosphors, the final stage of the topic is scheduled to test the core-shell nanostructures in photodynamic therapy of cancer. One of the most effective upconversion nanocrystals $NaYF_4$:Yb^{3+},Tm^{3+} / Er^{3+} will be used as the "core", and as for "shell" a relatively new class of cationic/metal porphyrins with a high quantum yield of reactive oxygen species, including singlet oxygen one.

It is also planned to create a single and complementary optical platform for selective imaging/bioimaging of samples under study using nonlinear Raman microscopy and upconversion luminescence effect as well.

Thus, the proposed theme research programme is in line with the modern and innovative world trends in the development of non-linear modalities of Raman spectroscopy, aimed, among other things, at the spectroscopy of single molecules, as well as photo- and upconversion luminescence of phosphors based on promising and advanced "core-shell" nanostructures.

The work on the whole will be carried out by the team of the Raman spectroscopy sector of FLNP comprising two groups, in close cooperation with a number of interested partners from various scientific and educational institutions and organizations, primarily from the JINR Member States.

Project:

"**Ultrasensitive SECARS microspectroscopy and luminescent core-shell nanostructures"**

Project leaders: G.M. Arzumanyan, N. Kučerka

Project deputy leader: K. Mamatkulov

List of activities

1. Development of scientific and technical requirements for the hardware and software upgrade of the "CARS" microspectrometer under the ultrasensitive modality SECARS.
2. Study of spectral and plasmonic characteristics of SERS-active substrates based on silver and gold nanoparticles with different configurations.
3. Revealing of the nature of nonresonant background of SECARS signal and development the ways to suppress it.
4. Systematic experiments on SECARS spectroscopy and SECARS intensity mapping with picosecond laser pulses at SERS-active substrates.
5. Detection of extremely low concentrations of organic molecules in SECARS mode – microspectroscopy of single molecules.
6. Development of theoretical model of SECARS maps of the intensity.
7. Study of spectral-structural characteristics of up-conversion phosphors based on "core-shell" type of nanostructures.

8. Development of the concept of a united optical platform for a contrast bioimaging of samples using nonlinear Raman microscopy and upconversion luminescence.
9. Test application of luminescent nanostructures "core-shell" in biomedicine, in particular, in photodynamic therapy of cancer.
10. Verification of tumor and stem cells by Raman microspectroscopy.
11. Extension of the “CARS” microscope operation program as a "user friendly facility".

Expected main results upon the theme completion:

1. The establishment of upgraded optical platform for ultrasensitive spectroscopy SECARS.
2. Selection of the optimal for their spectral and plasmonic characteristics of SERS-active substrates for a surface-enhanced CARS process.
3. Reproducible detection of organic single/unit molecules Raman scattering spectra with SERS and SECARS.
4. A theoretical model of the nonlinear interaction of picosecond pulses with analyte molecules adsorbed on SERS-active substrates (SECARS intensity map modeling).
5. Spectral and structural characteristics of “core-shell” upconversion phosphors with various rare earth elements located in their core.
6. Operation of unified optical platform for complementary bioimaging in two options: nonlinear Raman microscopy and upconversion luminescence.
7. Identification of the effectiveness of the use of cationic / metal-porphyrins as shells, and nanocrystals $NaYF_4$: Yb^{3+}, Tm^{3+} / Er^{3+} as a core, in photodynamic therapy of cancer.
8. Data on similarities and differences in Raman spectra of rat/mouse brain tumor cells and stem cells (non-tumor cells). Recommendations based on the obtained results.

Collaboration:

Armenia (Yerevan, Inst. of biochemistry), Belarus (Minsk, Inst. of physiology, BSUIR, “SOL Instruments”), Bulgaria (Sofia, Inst. of microbiology), Germany (Jülich, FZJ), Latvia (Riga, ISSP, Lat. Univ.) Poland (Wroclaw Univ., Poznan, Adam Mickiewicz Univ.), Russia (Moscow, GPI RAS, MSU), Slovakia (Košice, Pavol Jozef Safarik University), Ukraine (Donetsk nat. Univ.), United Kingdom (Buckingham, Centre of astrobiology).

Terms of the theme implementation: **January 2018 – December 2020**

Total estimated cost of the theme implementation according to JINR's Seven-Year Plan:

YEAR	k$
2018	153
2019	163
2020	174

AGREED:

Chief scientific secretary of JINR

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“____” _____2017

Head,
Planning and Finance Department

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“____” _____2017

Head,
Science Organization Department

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“____” _____2017

Director of FLNP

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Scientific secretary of FLNP

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Economist of FLNP

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Team leaders

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