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Diagnosis and visualization of cancer using resonant energy transfer in immunocomplexes of single-domain and full-sized antibodies

A. V. Baranov\textsuperscript{a}, A. V. Fedorov\textsuperscript{a}, A. Sukhanova\textsuperscript{b,c} and I. R. Nabiev\textsuperscript{b,c}

\textsuperscript{a}ITMO University, Saint Petersburg, Russia
\textsuperscript{b}Laboratoire de Recherche en Nanosciences, LRN-EA4682, UFR de Pharmacie, Université de Reims Champagne-Ardenne, Reims, France
\textsuperscript{c}Laboratory of Nano-Bioengineering, Moscow Engineering Physics Institute, National Research Nuclear University MEPhI, Moscow, Russia

a_v_baranov@yahoo.com

The report presents data on the development of a system for the early diagnosis and imaging of lung cancer and breast cancer while providing increased sensitivity for the detection of tumor markers compared to existing photon diagnostic methods. As elements of the system, we use the conjugates based on fluorescent semiconductor nanocrystals - quantum dots (QDs) CuInS\textsubscript{2} / ZnS, which have several advantages as fluorescent labels compared to traditionally used organic dyes, as well as tumor marker-specific single-domain antibodies and full-sized primary antibodies.
Entrapment of enzymes within magnetic porous matrices: towards stimuli-responsive biosystems

A. S. Drozdov, Y. Andreeva, K. Shinkar, D. Avnir, and V. Vinogradov
ITMO University, SCAMT Institute, Saint Petersburg, Russian Federation

droz dov@itmo.ru

Hybrid enzymatic nanocomposites are the perspective class of materials that are used to catalyze biological processes and can be used in different fields of industry and medicine. Such materials are combining both high catalytic rates and selectivity inherent to enzymatic systems with stability and responsiveness to physical stimuli due to presence of nanoparticles. These properties allow using such materials in extreme conditions inaccessible to free enzymes, such high temperatures, extreme pH values or presence of oxidizing agents. Responsiveness to physical stimuli allows manipulating hybrid enzymatic composites in order to increase their local concentration, to perform magnetic separation, or modulate their catalytic activity under the influence of electromagnetic irradiation of different natures, such as UV/VIS light, electric fields or alternating magnetic field.

Recently we have described a magnetite hydrosol capable of undergoing room-temperature sol-gel transition. The hydrosol consisted of electrostatically stabilized pristine magnetite nanoparticles dispersed in water media at neutral pH and without any polymers or surfactant molecules. The hydrosols are showing excellent colloidal stability with a shelf life over three months and behaving as magnetic fluid demonstrating magneto-rheological effects. Such systems can be condensed at room temperature to form mesoporous xerogels or hydrogels and can be used or entrapment of a variety of organic molecules, proteins, or enzymes. The entrapped proteins and enzymes not only conserve their catalytic properties but also demonstrating increased temperature stability and can be used for therapeutic applications to fight cardiovascular diseases. Moreover, the catalytic activity of such systems can be modulated by application of a high-frequency magnetic field. For instance, the reaction rate of CAB@magnetite composites can be increased up to 457% of its initial value at the AC field frequency 210 kHz and...
amplitude 937 A/m⁴. Reaction rate acceleration is fully reversible and demonstrates a fast response to the applied field. Such hybrid materials can find their application for drug delivery systems with controlled activity design, creation of magnetically-responsive biosystems and nano-biorobotics.

**Figure 1.** Magnetite hydrosol (a); SEM image of sol-gel magnetite matrix (b); TEM image of sol-gel magnetite (c); a schematic representation of an enzyme entrapped in sol-gel magnetite (d).

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**References**

Amino functionalization of carbon dots for red emission enhancement

E. V. Kundelev, V. G. Maslov

ITMO University, Saint Petersburg, Russia

kundelev.evg@gmail.com

Finding a synthetic route to carbon dots (CDots) with bright red photoluminescence (PL) will significantly advance their biological and optoelectronic applications. Current synthesis techniques can only yield CDots with either strong blue or weak red PL.

We showed that amino functionalization of CDots shifts their PL to longer wavelengths without reducing its quantum yield\(^1\). We built a simple model of amino-functionalized CDots by assuming that their optical response is mainly determined by molecule-like subunits forming the CDot’s surface\(^2\). The excited state of the subunits is characterized by strong charge separation between the amino groups and the carbon core of the CDot. This separation leads to the Stokes shift of the CDots’ PL, which grows with the functionalization degree of the CDots. By considering different functionalization degrees of the subunits constituting CDots, we showed that the PL spectrum strongly depends on the excitation wavelength, exhibiting a trend observed earlier for nitrogen CDots. Our work is intended to lay the theoretical foundation for guiding future development of ultrabright red-emitting CDots.

References

Slow light resonant structures due to nanoscale variations of an optical fibre surface

N. A. Toropov

Aston University, Birmingham, United Kingdom

nikita.a.toropov@gmail.com

Microresonators are often considered as the key elements of photonic integrated circuits with applications in telecommunications, classical and quantum optical signal processing, and ultraprecise sensing, especially in biosensing. In particular, microresonators are the necessary components of miniature slow light devices, namely, miniature optical delay lines and buffers. In the past decade, many approaches for fabrication of these devices were implemented, e.g. those based on coupled ring resonators and photonic crystals. However, the remarkable fabrication precision of a few nanometres achieved in silicon photonics is still way insufficient for the fabrication of realistic miniature low-loss delay lines. In addition to high insertion losses and insufficient fabrication precision, slow light devices fabricated to date experience additional physical limitations having significant signal dispersion and narrow bandwidth. The techniques for fabrication of microresonators are also very relevant for single-molecule detection.

In the first part of the talk, we discussed how to fabricate two coupled high $Q$-factor WGM microresonators at the fibre surface with resonances that are matched with a better than 0.16 GHz precision corresponding to a better than 0.17 Å precision in the effective radius variation of the fibre. The achieved precision is only limited by the measurement resolution of our spectrum analyser. In the second part of the report, we show that a WGM microresonator can be introduced temporarily by local heating of the fibre and maintain its shape with subangstrom precision for the predetermined period of time and be completely annihilated under request. In the third part of the report, we demonstrate WGM microresonators formed by mechanical bending of an optical fibre. We suggest that the developed method pave the way for the fabrication of ultralow loss, tunable, and reconfigurable microresonator-based photonic integrated circuits and biosensors.
Charge transfer between PbS quantum dots and MoS$_2$ nanoflakes

I. D. Skurlov$^a$, A. S. Mudrak, A. V. Sokolova, S. A. Cherevko, A. P. Litvin

$^a$ITMO University, Saint-Petersburg, Russia

sky_id@itmo.ru

Research in the area of two-dimensional nanomaterials has been reinvigorated after the graphene discovery. Monolayered transition metal dichalcogenides became a promising material for electronics and photonic applications. When TMD thickness approaches the monolayer limit, energy levels structure of the TMD drastically changes. Namely, MoS$_2$, indirect bandgap semiconductor became direct bandgap semiconductor, thus enabling its photoluminescence. However, thin layers of TMDs has been usually obtained via epitaxial methods, which are costly and complicated. Right now, it is possible to obtain nanosheets or nanoflakes of TMDs via different exfoliation methods. This opens the way to solution processing of the TMDs, enabling easier device fabrication.

**Figure 1.** Schematic illustration of charge transfer from QD to the MoS$_2$ nanoflake.

PbS quantum dots possess high absorption in the NIR and can be used to generate electron-hole pairs. Such electrons and holes might be transferred to the MoS$_2$ (the process is schematically displayed in Fig. 1). After that, the carriers can either radiatively recombine to emit visible photon or send an
electric response due the high conductivity of the monolayered MoS$_2$. In other words, utilizing charge transfer between QDs and TMD layer it is possible to create an efficient phototransistors or up-conversion emitters.

In our work we study the charge transfer between PbS QDs and MoS$_2$ nanoflakes. The first crucial parameter is the distance between QDs and the MoS$_2$ nanoflake. We investigate the impact of the distance by changing the ligand shell of the QD. The second parameter is the size of the QD, which directly govern its properties.

References

Investigation of the effect of active laser drug delivery and PDT on its absorption spectrum

A. V. Belikov, A.D. Tavalinskaya, Y.V. Semyashkina, and S.N. Smirnov
ITMO University, Saint-Petersburg, Russia
ntavalin@gmail.com

At present, onychomycosis (fungal infection) is a widespread disease [1], and the search for effective methods of its treatment remains an important problem in dermatology. Local therapy of nail diseases is limited by the low permeability of the nail plate for drugs due to the high density of keratinocytes in its composition\(^1\). The permeability of the nail plate can be increased using laser microperforation\(^2\). Drug delivery can be passive or active, i.e. occur without or as a result of any external influence. However, with passive delivery, water-based drugs do not penetrate the perforated nail plate due to the high surface tension coefficient\(^2\). It was established that laser-induced hydrodynamic processes (a kind of active delivery) can increase the rate of penetration of drugs into biological tissue\(^3\).

The purpose of this study was to estimate the influence of Er:YLF-laser radiation during active delivery of photosensitizer (1% solution of methylene blue) on its extinction spectrum in the range of 350-900 nm. The influence of photodynamic therapy (PDT) on extinction spectrum of methylene blue, “Revixan” gel (Areal LLC, Russia) and “Chloderm” (Chloderm TM, Russia) was also established. All these photosensitizers are widely used for photodynamic therapy of fungal diseases.

Er:YLF-laser active drug delivery was modelled in our experiments as a laser action on a drug drop with different exposure parameters – laser pulse energy and number of pulses.

The changes in extinction spectra observed after drug delivery and/or PDT were associated with conformation of photosensitizers. The change in the intensity of characteristic bands in the extinction spectra and their shift were examined. These changes indicate conformational rearrangements in the photosensitizer molecules and changes in their functional characteristics.
It was found that after active laser drug delivery the absorption band of methylene blue shifts in the long-wavelength region, which may be associated with the transformation of the molecules. In addition, after laser delivery, the extinction coefficient increases, which may relate to an increase in the drug concentration due to an evaporation of water (drug base). After PDT, the decrease in extinction coefficient (bleaching) of photosensitizers associated with the destruction of molecules was observed.

References
1. S. Murdan, Enhancing the nail permeability of topically applied drugs, Expert opinion on drug delivery. 5 (11), 1267-1282 (2008).
Ionizing radiation is widespread in power engineering, industry, and medicine. Radiation detection and measurement play an important role in these applications. Recently, semiconductor quantum dots have attracted attention as sensors of ionizing radiation: they can detect various kinds of ionizing radiation in the dose range from tens to hundreds Gy. Radiation detection can be based on qualitatively different effects: scintillation upon irradiation or radiation-induced luminescence quenching. In the present paper, radiation-induced quenching of CdSe/ZnS quantum dots fluorescence was studied under photon irradiation. The concentration of quantum dots in hexane solution was 1.3 mg/ml; irradiation was performed using 6 MeV Varian Trilogy linac. We found that exposure to 25-265 Gy leads to a significant decrease in the fluorescent intensity of quantum dots solution. More than 2-fold decrease in fluorescence was observed at 25 Gy, and only ~17% of the initial signal amplitude was recorded at exposure of 265 Gy. Irradiation did not cause changes in the colloidal stability of the quantum dots; measurements were performed using dynamic light scattering technique. Thus, semiconductor quantum dots have demonstrated the possibility of detecting high-energy photon radiation with a high degree of sensitivity.
Surface-Enhanced Near-Infrared Spectroscopy with Plasmonic Nanoantennas

D. R. Dadadzhanov\textsuperscript{a,b}, T. A. Vartanyan\textsuperscript{a}, and A. Karabchevsky\textsuperscript{b}

\textsuperscript{a}ITMO University, Saint-Petersburg, Russia
\textsuperscript{b}Ben-Gurion University of Negev, Beer-Sheba, Israel

daler.dadadzhanov@gmail.com

Near infrared (NIR) spectroscopy would be a technique of choice for identification of organic molecules and molecular constituents if the absorption bands corresponding to the resonant excitation of the dipole-active overtones of molecular vibrations is not so much weaker than the fundamental bands lying in the mid-infrared range\textsuperscript{1}. To overcome this limitation several approaches were put forward. Those that are based on the application of localized plasmon excitations metal nanoparticles were especially successful. Noble metal nanoparticles exhibit plasmon resonance due to the collective oscillation of free conduction electrons that are in resonance with the incidence light\textsuperscript{2}. Application of plasmonic nanoparticle in the NIR spectroscopy has led to the development of a number of techniques known as surface-enhanced fluorescence (SEF), metal-enhanced fluorescence (MEF), surface-enhanced infrared absorption (SEIRA) and surface-enhanced near infrared absorption (SENIRA). Besides of that, they demonstrate the lightning rod effect thus, playing the role of a nanoantenna. These properties may be employed to amplify the light-matter interaction in the NIR range where the overtone molecular vibrations are situated. Thus, the surface enhanced near-infrared spectroscopy makes it possible to detect molecular vibrations in NIR region with high sensitivity. Taking into account the variety of phenomena that occur in the course of metal nanoparticle – molecular interaction, further development of the ideas presented above is highly required.

Here we report on the influence of near field coupling of plasmonic gold nanoantenna and weakly absorbing media on the optical properties of the combined system in the NIR range. We calculated transmission and reflection sections spectra of gold nanoantennas array of different length arranged on BK-7 substrates as indicated in Figure 1 (A, C). A derivative of anilines molecule, namely, N-methylaniline (NMA) has been used as a probe analyte.
Optical properties of NMA first-order overtone transitions bands corresponding to aryl N-H and C-H bands obtained in\textsuperscript{3} were used in the simulations. The SENIRA activity of gold periodic array with fixed periods ($\Lambda_1=400$ nm and $\Lambda_2=200$ nm) has been numerically evaluated as shown in differential transmission spectra in Figure 1 (C). By leveraging the strong electromagnetic field enhancement of plasmonic nanoantennas and the “lighting rod effect” up 6-fold enhancement of absorption in the range of first-order overtone bands with the respect to bare NMA layer of the same thickness has been achieved.

![Figure 1](image)

**Figure 1.** (A, B - top and side view) The sketch of the geometry of plasmonic nanoantenna array with grating periods $\Lambda_1, \Lambda_2$. The nanoantennas have the fixed width $W=20$ nm and variable length $L$ encoded in the plot by the color of the curves. The NMA layer thickness was set for $t=100$ nm. (C) The differential transmission spectra of arrays of plasmonic nanoantennas of varied length $L$ covered with thin NMA layer

The obtained results demonstrate the ability to develop a tool for studying of vibrational spectra, thereby expanding the fundamental spectroscopic knowledge, as well as for label-free detecting of weakly absorbing analyte molecules.

**References**

Tuning the Physiochemical Properties of 2D Materials for Energy Storage Applications

Chandra Sekhar Rout
Centre for Nano & Material Sciences, Jain University, Jakkasandra Post, Kanakapura Taluk, Ramanagara District-562112, Karnataka, India
csrout@gmail.com

The ever-growing global demand of energy together with the depletion of fossil fuels makes it critical to develop sustainable and renewable energy resources. Developing relevant energy storage systems such as supercapacitors and batteries is essential to utilizing sustainable and renewable energy resources. Supercapacitors store energy in terms of both electrostatic double layer capacitance (EDLC) and pseudocapacitance. Nanostructured hybrid materials with both organic and inorganic components have attracted much attention recently due to the possibility of tailoring their dimensionality to facilitate a change in their fundamental properties including redox potential, conductivity and charge storage, in comparison with those of their bulk analogs\textsuperscript{1-5}. In my talk, I’ll discuss the working principles and fundamental aspects of supercapacitors and the recent achievements of our research group on design of 2D layered materials and nanocarbon hybrids for supercapacitor applications\textsuperscript{1-5}. In one of our work, we have reported the concatenated structure of metallic VSe\textsubscript{2} and multi-walled carbon nanotubes (MWCNTs) based hybrid materials for high performance energy storage and high power operation application (Fig. 1). The dominance of capacitive energy storage performance behaviour of VSe\textsubscript{2}/MWCNTs hybrids is observed. We have studied electrochemical supercapacitor performance of VSe\textsubscript{2}-reduced graphene oxide (RGO) hybrid for the first time which will be highlighted\textsuperscript{6}. The hybrid was synthesized via one-step hydrothermal route at different concentrations of graphene oxide, i.e. 0.15, 0.3, and 0.75 wt\%. Enhanced supercapacitor performances were observed in the case of the hybrid obtained with 0.3 wt\% of GO. It showed a specific capacitance of \( \sim \)500 F/g at current density of 1 A/g which was \( \sim \)3 and \( \sim \)12 fold higher than bare VSe\textsubscript{2} and bare RGO, respectively. Furthermore, high energy density of \( \sim \)156 Wh/kg and power density of \( \sim \)924 W/kg was obtained for the hybrid material. Also, the effect of nanostructures on the properties of supercapacitor performances
including specific capacitance, rate capability, energy density, power density and cycle stability for the next generation of supercapacitor electrode design will be discussed.

Figure 1. VSe$_2$ based 2D materials for energy storage applications: (a) Low and (b) high magnification FESEM images of pristine VSe$_2$ nanosheets, (c) Low and (d) high magnification FESEM images VSe$_2$/MWCNTs composite, (e-h) elemental mapping of VSe$_2$/MWCNTs.

References

Holographic grating relaxation technique for soft matter studies and development of selective optical elements

A. V. Veniaminov

aITMO University, St. Petersburg, Russia

avveniaminov@itmo.ru

The grating relaxation technique (GRT), also known as holographic relaxometry\(^1\) and forced Rayleigh scattering\(^2\), is the research tool for the study of various relaxation processes, mass and heat transfer, photo- and dark transformations, based on monitoring the light diffracted by periodic structures imprinted in the specimen of interest – in other words, simple holograms recorded in it. Unlike other holographic methods, GRT neither records information patterns nor creates diffraction optical elements, but due to spatial period variable from subwavelength to almost macroscopic values it is suitable for detection and investigation of otherwise inaccessible especially slow and anomalous diffusion in heterogeneous viscous media\(^3\): measurement of diffusion and drift as slow as \(10^{-3} \text{ nm}^2 \text{s}^{-1}\) and \(10^{-4} \text{ nm} \cdot \text{s}^{-1}\), respectively, is feasible, and relaxation spectra spanning over 8 decimal orders can be extracted from kinetic data. The information obtained using the GRT technique has made it possible to develop novel extremely selective and efficient holographic optical elements for spectroscopy and laser detection and ranging applications\(^4\).

References

Synthesis of Calcium Carbonate Particles with Different Geometries

L.I. Fatkhutdinova\textsuperscript{a}, H. Bahrom\textsuperscript{b}, A.A. Goncharenko\textsuperscript{c}, O. Peltek\textsuperscript{a},
A. Muslimov\textsuperscript{d,e}, A. Manchev\textsuperscript{b}, I. Shishkin\textsuperscript{a}, R.E. Noskov\textsuperscript{b}, A. S. Timin\textsuperscript{c,f},
P. Ginzburg\textsuperscript{b}, M.V. Zyuzin\textsuperscript{a}

\textsuperscript{a}ITMO University, Saint Petersburg, Russian Federation
\textsuperscript{b}Tel-Aviv University, Tel-Aviv, Israel
\textsuperscript{c}Peter the Great St. Petersburg Polytechnic University, Saint Petersburg, Russian Federation
\textsuperscript{d}St. Petersburg Academic University, Saint Petersburg, Russian Federation
\textsuperscript{e}I.P. Pavlov State Medical University, Saint Petersburg, Russian Federation
\textsuperscript{f}National Research Tomsk Polytechnic University, Tomsk, Russian Federation

landysh.fatkhutdinova@gmail.com

Nano- and microparticles are extensively used in different fields of science. In modern pharmacology and nanomedicine, nanoparticles can be applied for drug delivery due to their unique physicochemical properties. Particles of nano- and micrometric sizes with required properties such as biocompatibility, non-toxicity and high loading capacity are of great interest and can be utilized as carriers of bioactive compounds.\textsuperscript{1}

Porous calcium carbonate (CaCO\textsubscript{3}) particles require all above mentioned properties and are widely used due to their simple and low-cost synthesis, biocompatibility, and bioavailability.\textsuperscript{2}

Here, we study the formation of CaCO\textsubscript{3} particles, as well as the possibility of using them for biomedical applications.\textsuperscript{3}

The formation of CaCO\textsubscript{3} particles occurred in precipitation reaction of calcium chloride and sodium carbonate. The conditions of the formation of three existing polymorphic phases of CaCO\textsubscript{3} (calcite, vaterite, aragonite) were investigated. To obtain different geometries (spheroids, ellipsoids, toroids) of CaCO\textsubscript{3} particles, ratios of salts and organic additives in co-precipitation reaction were varied. The loading capacity and the internalization efficiency of the obtained particles was tested on the model of C6 glioma cells. Schematic illustration of the synthesis of CaCO\textsubscript{3} particles with different geometries is depicted in Fig. 1.
According to the obtained data, it was found that the polymorphic modification of CaCO₃ depends on the concentration of salts used for the synthesis. Also, all samples demonstrated good biocompatibility and non-toxicity. In particular, toroidal CaCO₃ particles showed the highest loading capacity of bioactive molecules, whereas the ellipsoidal particles demonstrated the highest internalization rate into C6 glioma cells. Therefore, nano- and micrometric CaCO₃ particles of different geometries can be considered as good candidates for the delivery bioactive compounds into cells.

![Schematic illustration of synthesis of CaCO₃ particles with different geometries.](image)

**Figure 1.** Schematic illustration of synthesis of CaCO₃ particles with different geometries.

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**References**


Photophysical properties of hybrid structures based on Semiconductor Quantum Dots and multilayered Graphene Nanobelts

I. A. Reznik\textsuperscript{a}, D. Silva de Lara\textsuperscript{b}, R. Savu\textsuperscript{b}, S.A. Moshkalev\textsuperscript{b} and A.O. Orlova\textsuperscript{a}

\textsuperscript{a}ITMO University, Saint Petersburg, Russia
\textsuperscript{b}University of Campinas, Campinas, Brazil

ivanreznik1993@mail.ru

Maintaining the photostability of systems based on quantum dots (QDs), i.e. stability of nonradiative rate of electron relaxation in QDs, is one of the most demanding issues of QD based photovoltaic devices\textsuperscript{1}. The main bottleneck in most of already proposed solutions to this problem is a poor understanding of how many pathways of electron relaxation exist in QD based nanostructures and how their rates correlate to each other. Here we discuss what electron relaxation pathways have a high probability in multilayered hybrid structures based on CdSe/ZnS QDs and Graphene nanobelts. We have taken into account the multiexponential excitonic PL decay of QDs that is caused by so-called blinking effect and that depends on QD immediate environment and an external irradiation dose.

The photoluminescent and photovoltaic properties of hybrid nanostructures based on a monolayer CdSe/ZnS core/shell quantum dots with 5.5 nm average core size and multilayer Graphene nanobelts formed on a Field Effect Transistor (FET) substrate, have been analysed to estimate the energy/charge transfer efficiency from QD to Graphene. The hybrid structures were irradiated with 405 nm LED that absorbed efficiently by QDs using different FET substrate back gate voltage.

The analysis of PL kinetics of QDs in the hybrid structures has shown that photostability of the hybrid structures demonstrates sharp dependence on charge carriers concentration in QDs and Graphene nanobelts because it modulates the efficiency of charge transfer between QDs and multilayered graphene.

References

Photophysical properties of InP QDs inside and outside cultured cells

I. K. Litvinov\textsuperscript{a}, E.A. Leontieva\textsuperscript{a}, A.O. Orlova\textsuperscript{b}, E.S. Kornilova\textsuperscript{a,c}, T.N. Belyaeva\textsuperscript{a}

\textsuperscript{a}Institute of Cytology of the Russian Academy of Sciences, St. Petersburg, Russia
\textsuperscript{b}ITMO University, St. Petersburg, Russia
\textsuperscript{c}Peter the Great St. Petersburg Polytechnic University, St. Petersburg, Russia

lik314@mail.ru

The development of modern approaches for medical diagnostics and visualization of biological processes is aimed at creating multi-functional platforms. For these purposes, semiconductor quantum dots (QDs) seem to be the most promising. The uniqueness of QDs is determined by such properties as a wide absorption spectrum, narrow luminescence spectra, depending on the size of the QDs, large Stokes shift, and high quantum yield. For biological studies, core/shell QDs are most often used, and to ensure biocompatibility they are coated with organic molecules. The presence of the shell also allows the modification of QDs in such a way as to provide specific binding to biological targets. Currently, the most commonly used are QDs based on CdSe/ZnS coated with PEG with various active groups. Since Cd is a toxic element, the use of such QDs is problematic because of the possibility of damage to the core of the QDs and the release of ions from the composition of the QDs. However, data on their cytotoxicity in the literature are highly controversial. Nevertheless, to exclude the possible effect of Cd\textsuperscript{2+} ion leakage, we investigated the interaction with cells of non-targeting cadmium-free QD based on InP/ZnS, which are considered less toxic.

It is important to note that the structural integrity of QDs and, as a result, the photophysical properties can change under the influence of various
environmental factors (ions of various compounds, pH level, etc.), which is significant in assessing the efficiency of their absorption by cells. Previously, in our studies, it was shown that QDs based on CdSe/ZnS and coated with L-cysteine undergo changes in photophysical characteristics when they enter the cells. Thus, a decrease in the luminescence lifetimes of QDs by 30–35% in cells was observed, compared with the data on the luminescence lifetimes of QDs in the DMEM nutrient medium and by 70–75%, compared with the luminescence lifetimes in water¹.

In the present work, InP / ZnS-PEG-COOH QDs were analyzed. The study used cell cultures of the HeLa and A⁵49 lines. The work was carried out using a MicroTime 100 laser scanning fluorescence microscope (PicoQuant). To analyze the kinetics of luminescence decay, a multi-exponential model of QDs luminescence decay was used². It was found that the average lifetime of QDs luminescence in water was about 50 ns. After incubation of QDs with cells for 24 h, a significant part of QDs was detected in intracellular structures, but part of the QDs formed clusters on the surface or outside the cells. It was found that the luminescence lifetimes of QDs inside the cells are reduced to 20–25 ns and outside the cells to 30–40 ns, which corresponds to the values of the luminescence lifetimes of InP/ZnS QDs in DMEM nutrient media. The revealed differences indicate that both the extracellular medium and the intracellular microenvironment of QDs affect their luminescent properties.

This work was financially supported by the program of the Presidium of the Russian Academy of Sciences No. 32 “Nanostructures: Physics, Chemistry, Biology, Technology Basics”, the grant of the Russian Foundation for Basic Research No. 18-34-00382 and by Government of Russian Federation, Grant 08-08.

**References**


The influence of curcumin on the electrospun fibers based on hyaluronic acid

P. P. Snetkov$^a$, S. N. Morozkina$^a$, M. V. Uspenskaya$^a$, R. O. Olekhnovich$^a$

$^a$ITMO University, Saint Petersburg, Russian Federation

ppsnetkov@itmo.ru

Both modern biomedicine and pharmacology need the effective regenerative materials and drug delivery systems. One of the most attractive issues is the obtaining of the nano- and microfibrous materials based on biopolymers: chitosan, hyaluronic acid, silk fibroin, etc. Such materials could be an individual wound healing materials itself, but pharmacological substances in the polymer matrix increases the effectiveness of the material. Moreover, the materials contained natural biologically-active agents are preferable than these ones with synthetic drugs due to low toxic effects of natural components.

Hyaluronic acid having the hydrophilic nature is the most advanced biopolymer which is utilized as biocompatible and biodegradable matrix for the pharmacological substances having, in general, hydrophobic nature. Note, that aqueous hyaluronic acid solutions have a high viscosity and surface tension, low evaporability, which hinder the electrospinning process being an effective and accessible method for fiber formation.

Despite of the high levels of viscosity and surface tension of hyaluronic acid solution, in our previous study$^1$ the polymer particles and fibers based on hyaluronic acid were successfully obtained. Note, that additional polymers (named “initiators” of electrospinning process), such as polyvinyl alcohol or polyethylene oxide, were not utilized. The binary solution system contains only distilled water and dimethyl sulfoxide (DMSO) with volume ratio 50:50. The using of DMSO allows to obtain non-toxic and biodegradable materials for wound healing and tissue engineering.

For further research curcumin having anti-inflammatory, anti-bacterial and anti-tumour properties$^2$ was utilized. The stable soluble complex was obtained without the utilizing of the activating (catalyzing) agents$^{3-4}$ such as 1,3-dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopiridine (DMAP).
Curcumin addition improved the electrospinning process: the Taylor cone was more stable than without curcumin. The fibers with curcumin have wider diameter distribution (Table 1).

**Table 1.** Characterization of fiber obtained and electrospinning process

<table>
<thead>
<tr>
<th>Curcumin</th>
<th>Diameter of fibers obtained (nm)</th>
<th>Characterization</th>
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<tr>
<td></td>
<td>Min</td>
<td>Max</td>
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<td>-</td>
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<td>+</td>
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The electrospun fibers based on hyaluronic acid and the influence of curcumin on electrospinning process and fiber morphology will be discussed in this report. Curcumin containing fibers based on hyaluronic acid are obtained for the first time, and it opens their application as modern materials for tissue engineering and drug delivery systems.

The reported study was funded by RFBR, project number 19-33-90098.

**References**
Carbon nanotubes-based magneto-optically tunable structure for terahertz wave polarization control

A. Kvitsinskiy, P. Demchenko, E. Litvinov, M. Masyukov, I. Anoshkin, A. Vozianova, and M. Khodzitsky

aTerahertz Biomedicine Laboratory, ITMO University, Saint Petersburg, Russian Federation
bCenter for Bioengineering, ITMO University, Saint Petersburg, Russian Federation

anatolykvitsinskiy@gmail.com

Terahertz (THz) radiation is widely used in physics, medicine, chemistry, pharmacology, security systems and other fields of science. Currently, an important area of THz photonics is study of carbon nanotubes under an external optical pumping (OP) and an external static magnetic field (MF) to devise efficient tunable THz polarization modulators based on them.

The randomly oriented single-walled carbon nanotube (SWCNT) thin film on a silicon (Si) substrate (Fig. 1 (a–b)) and a sample of the Si substrate were studied. SWCNT thin film was synthesized on a nitrocellulose micropore filter by the catalytic ethanol-chemical vapor deposition1 at KTH Royal Institute of Technology (Sweden) and then transferred to a Si substrate with a surface area of ~1.0 cm² and a thickness of ~1.0 mm. SWCNTs diameters were calculated using the Kataura plot and were ~1.3–2.0 nm. SWCNTs length was visualized by the transmission electron microscopy and was ~15 μm. SWCNT film thickness was calculated from the optical absorbance at 550 nm and was ~110 nm. The high resistivity Si substrate was produced at Tydex (Russia).

The samples were studied using the THz-TDSP system² based on the THz time-domain spectrometer, two polarizers, 980 nm laser for creating an external OP of ~1.0 W/cm² and NdFeB axially magnetized magnet for an external static MF of ~1.3 T. For each sample, temporal waveforms of the transmitted THz signals under various external influences were recorded using LabVIEW® (United States) software at parallel and crossed by 45° positions to a transmission direction of the polarizers.
Figure 1. Scanning electron microscopy images of the top view of the SWCNT thin film on the Si substrate with the scale bars of (a) 10 μm, and (b) 1 μm; and frequency dependencies of (c) the azimuth angle $\psi$, and (d) the ellipticity angle $\chi$ of the polarization ellipse of the electromagnetic waves transmitted through the SWCNTs.

Frequency dependencies of the azimuth $\psi$ and the ellipticity $\chi$ angles of the polarization ellipse of the samples were calculated from the Stokes parameters (Fig. 1 (c–d)). The results confirm the fact that, based on SWCNTs, it is possible to devise efficient tunable THz polarization modulators for use in the biomedical research, and latest security and telecommunication systems. The reported study was funded by the Government of the Russian Federation, Grant Number 08–08 (Project 5–100).

References
Development of deoxyribozyme-based gene therapy against bacterial pathogens

A. V. Gertsen\textsuperscript{a}, K. P. Chalenko\textsuperscript{a}, D. M. Kolpashchikov\textsuperscript{a,b,c}, E. I. Koshel\textsuperscript{a}

\textsuperscript{a} Laboratory of Solution Chemistry of Advanced Materials and Technologies, ITMO University, St. Petersburg, Russian Federation
\textsuperscript{b} Chemistry Department, University of Central Florida, Orlando, USA
\textsuperscript{c} Burnett School of Biomedical Sciences, University of Central Florida, Orlando, USA

gertsen@scamt-itmo.ru

Antibiotic resistance is a widespread problem in the modern international health care system. Available drugs for the treatment of bacterial infections keep rapidly losing their effectiveness.\textsuperscript{1} The need for new approaches to solving this problem is greater than ever.

Deoxyribozymes (Dz) are DNA molecules with a catalytic activity that can cleave mRNA at specific sites.\textsuperscript{2} Dz already showed efficiency in cancer cells.\textsuperscript{3} Dz-based DNA-machines (DDM) can be used as new gene therapy agents.

Housekeeping gene \textit{infB} that encode translation initiation factor IF-2 of \textit{E. coli} was chosen as a target. Three Dz was designed to cleave the mRNA molecule of a gene at different sites. All of them showed effectiveness from 42 to 75 %. After that Dz was tested in pairs to choose the most efficient combination. Pair of Dz\textsubscript{1} and Dz\textsubscript{2} showed comparable cleavage activity to a combination of all three Dz.

Two different DNA – machines were designed based on a pair of Dz\textsubscript{1} and Dz\textsubscript{2}. Both DDM\textsubscript{1} and DDM\textsubscript{2} contain two Dz molecules conjugated through a platform. Not only didn't they abolish the catalytic activity of an enzyme, but both of them also demonstrated comparable efficacy. DDM\textsubscript{2} showed high activity with a cleavage rate at 79% since it was able to unwind the secondary structure. (Fig. 1) Having a shorter platform and annealing temperature closer to physiological conditions it was chosen for further revision.
Besides in vitro assay, all three Dz were tested ex vivo on a culture of *E. coli* strain Nova Blue. Since deoxyribozymes were not effective on chemically competent cells it was decided to stabilize them against nucleases attacks. The final design of the Dz molecule consists of 2'-O-methyl modified nucleotides in a catalytic core and phosphorothioate linkages between nucleotides in binding arms.

Our results indicate that deoxyribozymes show promising results as gene therapy agents. Our further direction is to create such DDM that would fight multidrug resistance bacteria by suppressing the expression of housekeeping genes in the presence of antibiotic resistance markers.

**References**

Quantum Dots for Biomedical Applications

A. O. Orlova

aITMO University, Saint-Petersburg, Russia

a.o.orlova@gmail.com

Colloidal CdSe quantum dots (QDs) are the eldest member of nanostructured phosphors that demonstrate strong absorption in a wide spectral range, bright photoluminescence with the narrow band, high chemical- and photostability\(^1\). Theoretical predictions claim that QDs are perfect energy and charge transfer donors in hybrid structures with different molecules and nanoparticles because their optical properties can be fine-tuned by adjustment of the QD core size and a type of semiconductor shell, spawning a new avenue in development of different nanostructured hybrid materials and device that can be used in biomedicine for theranostics and sensor applications\(^2\).

Some kinds of hybrid structures based on colloidal semiconductor QDs with tetrapyrrrole molecules, titania nanoparticles, and superparamagnetic nanoparticles developed in our group are discussed here. It is shown that optical and photophysical properties of QD based nanostructures strongly depend on their architecture and the type of organic stabilizers of QDs\(^3\)-\(^6\). It is also demonstrated that circular dichroism and magnetic circular dichroism spectroscopy are very sensitive techniques for monitoring of chiral properties and colloidal stability of QD hybrid structures, respectively\(^7\),\(^8\).

References

2. T. J. Wax, J. Zhao, Optical features of hybrid molecular/biological-quantum dot systems governed by energy transfer processes, JMCC. 7 (22), 6512-6526 (2019).
Introduction to CeramOptec products

P.A. Petrov\textsuperscript{a}, A.B. Griscenko\textsuperscript{a}, D.A. Saharovs\textsuperscript{a}

\textsuperscript{a}CeramOptec SIA, Livani, Latvia

petrovpa.c86@gmail.com

Synthetic quartz fibers and fluorine-doped reflective layer are widely used in the modern communication, industry\textsuperscript{1,2}, instrumentation\textsuperscript{3}, academic and scientific applications\textsuperscript{4}, and medicine\textsuperscript{5,6}. Hollow-core fibers are actively developing and exploring\textsuperscript{7}, as well as gas sensors on the plasmon effect\textsuperscript{8}.

Due to its physical and chemical properties, quartz fiber products are widely used in the evaporation operations of human body tissues and cosmetology. These products are also used in photodynamic therapy, for example for targeted activation of drugs\textsuperscript{9,10}. Due to the peculiarities of all these tasks, the development of fiber products for them, requires their deep understanding, and begins at the stage of selection of the material of glass blanks for alloying and fiber extraction.

In this presentation, the achievements of CeramOptec and the BioLitec group to which it is a part are briefly presented. CeramOptec SIA designs and manufactures fibers and fibers for industry, science and medicine and other applications. The BioLitec Group's activity covers the production of fiber and laser products for medicine from fiber manufactured by CeramOptec SIA. The focus of the presentation is on the medical application of fiber products, and the expansion of opportunities through nanotechnology and smart nanosystems.

References

Quantitative noninvasive characterisation of cell death process induced by intracellular generation of reactive oxygen species

A. V. Belashov\textsuperscript{a,b}, A. A. Zhikhoreva\textsuperscript{a}, T. N. Belyaeva\textsuperscript{c}, E. S. Kornilova\textsuperscript{c}, A. V. Salova\textsuperscript{c}, I. V. Semenova\textsuperscript{a}, O. S. Vasyutinskii\textsuperscript{a}
\textsuperscript{a}Ioffe Institute, Saint-Petersburg, Russia
\textsuperscript{b}ITMO University, Saint-Petersburg, Russia
\textsuperscript{c}Institute of Cytology of RAS, Saint-Petersburg, Russia

belashov.andrey.93@gmail.com

Photosensitized generation of reactive oxygen species (ROS) inside living cells of malignant tumors is a promising approach for cancer treatment\textsuperscript{1}. The method utilizes generation of highly toxic substance inside abnormal cells through optical excitation of photosensitizer molecules. In contrast with surgical treatment and chemotherapy, photodynamic treatment (PDTr) usually demonstrates low side effects and high efficiency in cancer cells, which can be achieved using quantum dots and specially developed and synthesized molecules aimed at increase of photosensitizer specificity to malignant tumors.

However particular mechanisms of ROS impact on living cells and cell death processes induced under photodynamic treatment are not well studied yet. One of the challenges arising in such studies is noninvasive long-term monitoring of photosensitized cells. Although the detection of specific fluorescent molecules such as annexin-V, propidium iodide or ethidium bromide is a robust technique for cell death monitoring, their noninvasive detection in photosensitized cells during long-term monitoring by fluorescence microscopy is somewhat difficult due to high sensitivity of photosensitized living cells to irradiation. Moreover, fluorescence microscopy does not provide quantitative data on cellular characteristics and cannot be used for quantitative assessment of cell death process.

In this report we present an alternative technique for cell death monitoring capable of quantitative description of optical, morphological and physiological parameters of cells. The method is based on the processing of
phase shift distributions induced by a living cell, obtained using digital holographic microscopy. Examples of phase images of HeLa cells recorded before and after PDTr at different doses are shown in Figure 1.

**Figure 1.** Examples of phase shift images of HeLa cells in the course of (a) apoptosis and (b) necrosis induced by PDTr.

In our study we have demonstrated that the analysis of the dynamics of cellular dry mass and average phase shift can be used for robust identification of cell death mechanism and quantification of its rate. In particular cells apoptosis is typically characterized by an increase of average phase shift, and no variation of cells dry mass. Meanwhile the necrosis type of cells death is featured by exponential decrease of both average phase shift and dry mass parameters. Moreover, average phase shift and dry mass decrease rate strongly depends on PDTr parameters, in particular on the irradiation dose and fluence rate. The suggested method can be useful for noninvasive quantitative assessment of PDT efficacy and resistivity of various types of cancer cells to certain types of photosensitizers.

This work was supported by grant #18-32-00364 from the Russian Foundation for Basic Research.

**References**

Carbon dot: Advancement towards understanding composition and optical properties

A. Das\textsuperscript{a} and P. Mandal\textsuperscript{b}

\textsuperscript{a}ITMO University, St. Petersburg, Russia
\textsuperscript{b}Department of Chemical Sciences, Indian Institute of Science Education and Research (IISER) Kolkata, Kolkata, India

prasunchem@iiserkol.ac.in

Since last a few years in fluorescent nanomaterial family a new member came with its unique own identity, named as carbon dot. This nanomaterial is gaining importance specially in biological field due to its non-toxic property.\textsuperscript{1} Generally, the PLQY of CDs is quite less in aqueous medium. Hereby, we have synthesised CDs with high PLQY (80\%) in aqueous medium.\textsuperscript{2} Properties like water solubility and high PLQY in aqueous medium make this CD a better optical probe for bio-imaging. However, the molecular origin of photoluminescence (PL) of CDs is not completely understood. Following rigorous analyses we could show that the molecular origin of PL for this CD is an aggregated 2-pyridone derivative.\textsuperscript{2} The average size of this CD is 8.3 nm and surface is negatively charged. Though the observation from rotational anisotropy decay with fluorescing unit size of $\sim$1.4 nm raises a serious question: whether the whole CD is fluorescing. Besides this we are able to show this CD acts as a donor in resonance energy transfer dynamics. In several nanomaterials questions regarding the applicability of Förster method towards RET have been raised. Following dynamical analyses we could show that Förster model can account for the observed experimental observables related to RET. These observations further enhance the potential of this particular CD towards bio-imaging.

References

Magneto-optical properties and photoactivation of core-shell-shell nanocomposites

A.A. Matushkina¹, I.A. Reznik¹, A.U. Dubavik¹, A.O. Orlova¹

¹ITMO University, Saint Petersburg, Russia

anyuta.matyushkina@mail.ru

Magneto-luminescent materials that do not exist in nature, can find numerous applications in the biomedical and environmental fields¹. Therefore, creation of a nanocomposite that simultaneously demonstrates bright luminescence and excellent magnetic properties is a burning task in modern nanotechnology. Here we describe magneto-optical properties of core-shell-shell nanocomposites comprised of a Fe₃O₄ supermagnetic nanoparticle covered with quantum-sized brightly luminescent CdSe layer, in its turn surrounded by ZnS passivating shell². Such an approach allows to obtain stable colloidal nanocomposites with well-controlled luminescent and magnetic properties. One of the key problems of classical semiconductor nanocrystals is the instability of their photophysical properties under the action of external photoirradiation³. Obviously, complex nanocomposites based on classical semiconductor materials can also be susceptible to this problem. In this case, the regularity by which photoactivation processes occur in nanocomposites that combine both quantum-sized luminescent semiconductors and paramagnetic materials are not known.

In this work, we studied the stability of the photophysical and magnetic properties of nanocomposites based on superparamagnetic Fe₃O₄ nanoparticles (SPIONs) and an outer quantum-well luminescent CdSe/ZnS shell. The growth of the CdSe semiconductor shell on SPIONs with an average size of 10 nm was accompanied by an increase in the size of nanocomposites to 13 nm, as well as the appearance of an exciton peak in the absorption spectrum of samples at 585 nm and a luminescence band with a maximum at 605 nm and a bandwidth of 34 nm. Subsequent growth of the ZnS shell increased the luminescence response of the sample (Fig. 1). The MCD spectra
of Fe₃O₄/CdSe/ZnS nanocomposites are characterized by the same transitions as the initial SPIONs.

Figure 1. The absorption (left) and luminescence (right) spectra of the samples

An analysis of the kinetics of the exciton luminescence of nanocomposites has shown that the decay of their luminescence is described by a three-exponential function with characteristic decay times equal to 0.7 ns, 6.0 ns, and 35.0 ns. As a result of sample irradiation with a total dose of 35 J, the characteristic luminescence decay times increased by 26, 39, and 11% for the short, medium, and long luminescent decay components, respectively. It indicates a successful photopassivation of the nanocomposite surface and an increase in their quantum yield of luminescence. Our results demonstrate that irradiation of Fe₃O₄/CdSe/ZnS nanocomposites by visible light absorbed efficiently by CdSe shell can improve significantly their luminescent properties while keeping their colloidal stability and magnetic properties.

References

Photophysical Properties of Hybrid Structures based on CdSe/ZnS QDs and Tetraphenylporphyrin in Organic Media

F. A. Sewid, and A.O. Orlova

aITMO University 1, St. Petersburg, Russia
bMansoura University 2, Mansoura, Egypt

fayzaomar8891@mail.com

Photosensitizers (PSs) are a special class of organic compounds that could induce a chemical change in another molecule during a photochemical process. Due to their unique properties and ability to generate reactive oxygen species (ROS), PSs have found a wide range of applications, the main of which include biomedicine, photovoltaics and photocatalysis.

Last decade, hybrid nanostructures based on PSs and various nanoparticles have been actively studied and demonstrated significant improvements in the functional properties of PSs and their colloidal stability. At the same time there are still several challenges that should be overcome, and one of them is aggregation of PSs in hybrid nanostructures. It was demonstrated that these processes could dramatically change the photophysical properties of PSs (e.g. reduce the efficiency of ROS generation by them). Therefore, in order to preserve and even enhance efficiency of PSs it is required to keep them in the monomeric form in hybrid nanostructures.

Quantum dots (QDs) are quasi-spherical semiconductor nanocrystals with a size of 2–10 nm. Their photoluminescence (PL) band position depends on QDs chemical composition and size. Now QDs have demonstrated some benefits as effective energy donors in composites with porphyrin molecules due to their unique optical and chemical properties.

We present the results of the study of hybrid nanostructures of CdSe/ZnS QDs with photosensitizer Tetraphenylporphyrin (TPP). QDs-TPP hybrid nanostructures have been formed and characterized by steady state absorption and PL spectroscopy combined with single photon correlation microscopy in chloroform. QDs-TPP hybrid nanostructures were formed
because of a reversible noncovalent self-assembly interaction of TPP meso-pyridyl nitrogens with ions of the ZnS shell of the CdSe/ZnS QDs.

Figure 1 shows the PL spectra of QDs and QDs-TPP mixtures. It is clearly seen that increase of TPP concentration in the samples leads to PL quenching of QDs due to efficient FRET from QDs. At low compound concentrations in our samples, i.e. $10^{-6}$ M, it indicates QDs-TPP hybrid nanostructure formation.

Figure 1. Luminescence spectra of CdSe/ZnS QDs-TPP hybrid nanostructures dissolved in Chloroform. Excitation wavelength is 460 nm

In the course of developing new efficient PDT drugs based on QDs, we are going to make fully biocompatible QDs-TPP hybrid nanostructures using chitosan molecules as stabilizing agent and test their impact in living cancer cells.

References
Using confocal microscopy to investigate the optical properties of c-dots.

V.V. Zakharov¹, M.S. Stepanova¹, P.D. Khavlyuk¹, A.Y. Dubavik¹,
E.V. Ushakova¹,², A.V. Veniaminov¹, A. L. Rogach¹,²

¹ITMO University, Saint-Petersburg, Russia
²City University of Hong Kong, Kowloon, Hong Kong

viktor-zah@yandex.ru

Carbon dots are a promising class of carbon-based fluorescent nanoparticles, the surface of which may contain functional groups. Carbon dots have several advantages, such as luminescence that can be rearranged along the wavelength, the availability and simplicity of synthesis, high photostability and biocompatibility with bioimaging potential [1-2].

Carbon dots were synthesized by the solvothermal method by dissolved citric acid and ethylenediamine in water. The sample was obtained by evaporation from a high-concentration aqueous solution of carbon dots and is a thin film. When a 405 nm laser light was applied to a 50x50 µm section of the sample, an increase in luminescence intensity and light transmission was observed.

Figure 1 (right) shows the luminescence spectra of the film areas from carbon dots before (1) and after (2) laser exposure. Along with a 2-fold increase in intensity, a shortwave shift of 50 nm in maximum luminescence is observed.

The change in intensity and the shift in the maximum luminescence spectrum during laser exposure are irreversible; they are supposedly caused by photo-influence on the internal structure of carbon dots. These processes do not depend on the ambient temperature and are not caused by the local heating of the area illuminated by the excitation laser. To confirm this, the optical properties of the obtained film in the temperature range from -200°C to 200°C were studied with the help of Linkam temperature-controlled cell.

The detected effect can be used to create thermostable fluorescent marks, the physical size of which is limited by the diffraction resolution of the optics (~ 200-300 nm) used for exposure.
Figure 1. Fluorescence image (left) and luminescence spectrum (right) of the carbon dots film before (1) and after (2) 405nm laser exposure.

References

The Effect of Ultrasound on the Optical Properties of Chlorin e6 in Melanoma Cells

A.I. Dadadzhanova¹, E.P. Kolesova¹, V.G. Maslov¹, J. Kost², A.O. Orlova¹

¹ITMO University, Saint Petersburg, Russia
²Ben-Gurion University of the Negev, Beer-Sheva, Israel

fadeeva.antonina95@gmail.com

The high incidence of oncology has reached alarming proportions and many methods are currently being developed to overcome this problem. There are several traditional ways to treat cancer, like chemotherapy, surgical removal, etc., each of which has side effects. Photodynamic therapy (PDT) is the well-known and popular type of oncology diseases therapy. It is based on the ability of photosensitizers, a special type of organic and inorganic species that can generate reactive oxygen species (ROS) efficiently under irradiation of the visible light and trigger apoptosis or necrosis of cancer cells. Despite clear benefits of PDT in comparison with other cancer treatment approaches, photodynamic therapy has one serious shortcoming, which limits its application. It is well known that PDT cannot be used to treat deeply localized tumors, since the depth of light penetration into the human body is not more than a few millimeters.

Recently it has been demonstrated that traditional photosensitizers exposed to ultrasound can impact strong apoptosis and necrosis effects in cancer cells. This approach to cancer treatment is called sonodynamic therapy (SDT)¹. This type of therapy resembles PDT, but ultrasound is used as an external effect, which has a depth of penetration into the human body much larger than that of light radiation. It should be pointed out that SDT effect is more complex because it results from the combination of different mechanisms. Today, cavitation effect and ROS generation by photosensitizers exposed to ultrasound are considered the most probable cancer cell killing mechanisms of SDT.

Tetrapyrrole molecules is a class of traditional photosensitizers used now as medicine in PDT and examined in SDT. It is well known that tetrapyrrole molecules tend to aggregate² that generally is accompanied by
drastically reduction of ROS generation by them because of breaking the Ermolaev–Sveshnikova rule. At the same time there are no direct data about the state of tetrapyrroles, i.e. the monomeric or some kind of aggregates, in cancer cells before and after light or ultrasound exposure.

The interaction of Chlorin e6 (Ce6) that represent tetrapyrrole molecules has been studied with melanoma A375 cells before and after ultrasound exposure. The analysis of optical properties of Ce6 in the melanoma cells presented in Figure 1 has clearly shown that the spectral positions of Ce6 first absorption band centered at 670 nm and the PL band centered at 675 nm, corresponds to Ce6 monomeric form. The ultrasound exposure on Ce6 in cells also does not lead to Ce6 aggregation. Our results clearly demonstrate that Ce6 is a perfect PDT and SDT medicine due to preservation of its monomeric form.

![figure1.png](attachment:figure1.png)

**Figure 1.** PL excitation and PL spectra (from left to right). Registration wavelengths: 700 nm for Ce6 in a nutrient medium and 740 nm for Ce6 in the cells. Excitation wavelengths: 435 nm for Ce6 in the nutrient medium and 405 nm for Ce6 in the cells.

**References**

Reusable SERS-substrate with silver plasmonic nanostructures for sensing application

K. Kirichek\textsuperscript{a}, D. R. Dadadzhanov\textsuperscript{a,b}, T.A. Vartanyan\textsuperscript{a}, I.A. Gladskikh\textsuperscript{a}, K.V. Bogdanov\textsuperscript{a}, R.D. Nabiulina\textsuperscript{a}, A.A. Starovoytov\textsuperscript{a}, M.A. Baranov\textsuperscript{a}, and A. Karabchevsky\textsuperscript{b}

\textsuperscript{a}ITMO University, Saint-Petersburg, Russia
\textsuperscript{b}Ben-Gurion University of Negev, Beer-Sheba, Israel

daler.dadadzhanov@gmail.com

Optical properties of noble metal nanostructures, in particular, gold and silver nanoparticle arrays used in surface-enhanced Raman scattering (SERS) is the active research field up to date despite their origin roots back to the 1970s\textsuperscript{1}. Distinctive features of such nanostructures rely on the locally enhanced electromagnetic field caused by localized surface plasmon resonance (LSPR). In order to increase the weak Raman signal, the analyte should be placed in the near field of metal nanostructures. Due to a giant amplification of the Raman signal, this approach makes it possible to identify the chemical structure of unknown analytes with high sensitivity unlike surface-enhanced fluorescence (SEF)\textsuperscript{2}. The main problems of SERS-substrates applied for sensing are their chemical stability and reusability. To overcome these problems and improve the performance of the SERS-based sensors, we proposed the fabrication approach based on the physical vapor deposition (PVD) of metal nanoparticles followed by thermal and laser treatments.

In this contribution we proposed a low-cost, highly stable, and reusable SERS-based sensors enabled by granulated silver nanostructures (Ag NS) prepared in PVD-75 (Kurt J. Lesker) vacuum chamber on glass substrates. The Ag NS was thermally annealed at 200 °C and then exposed to the pulsed laser irradiation at the wavelength of 355 nm. To this end the 3\textsuperscript{rd} harmonic of Nd: YAG laser (SolarLS, Minsk) was employed. The homological series of cyanine dyes (\textit{pseudoisocyanine} – Cy\textsubscript{1}, and \textit{dicarbocyanine} – Cy\textsubscript{5}) were sputtered on Ag NS /glass sample and bare glass sample using spin-coating method (SPIN150, SPS Europe). Fig. 1 plots the Raman spectra of thin layers of
cyanine dyes coated on top of Ag NS (1 – annealed, 2 – irradiated with low-laser fluence, 3 – irradiated with high-laser fluence) and on glass. The maximum enhancement factor (EF) of Raman intensity reaches 12 and 65, respectively. It was obtained in the case of annealed Ag/Cy1 and Ag/Cy5 samples. Unfortunately, these samples were prone to chemical instability and mechanical damage. The enhancement factors of illuminated substrate were somewhat lower, namely, 11 and 20. Nevertheless, their chemical and mechanical stability was greatly improved.

**Figure 1.** The Raman spectra of Ag/Cy1 and Cy1 (left), Ag/Cy5 and Cy5 (right). 1 - annealed, 2 - low-laser fluence, 3 – high laser fluence

In summary, the enhancement factor of SERS substrates was somewhat lowered after laser illumination. On the other hand, laser irradiation greatly improves their stability in organic solvents. The mechanical stability was also improved. Because of that the illuminated substrates possess definite potentials for applications in medical diagnostics, biological detection, etc.

**References**

Qualitative analysis of charged microparticles in a radio-frequency ion trap

A. V. Romanova, I. A. Kosternoi, and Y. V. Rozhdestvensky

ITMO University, Saint Petersburg, Russia

anromanna98@gmail.com

Electrodynamic ion trap is a tool that allows to confine the charged particles in a bounded region of space. Thus, localized particles can be non-destructively held for a long time what offers a promising field for studying their properties. These days three-dimensional confinement is implemented in vacuum using the laser cooling. However, this technique can be applied only to atomic and molecular ions in vacuum and method for studying biological objects in a medium is not developed yet. In the presence of medium a nonlinear term is added in motion equations. This term follows from the field nonlinearity which is deviation from configuration of an ideal quadrupole field or from nonlinear friction of the medium. As a result, a borderline between finite and infinite motion regions blurs and non-trivial stable solutions of motion equations appear. These solutions are called zero-crossing (ZC) or extended orbits for particles that move in a closed path in an ion trap. ZC-orbits differ from “classic” orbits in the absence of visible secular component and microoscillations what results in other oscillation frequency spectrum in comparison with vacuum localization or confinement in linear friction medium. Features of ZC-orbits depend on properties of localized particle including charge, mass and size, so an occurrence of certain dynamic behavior can be used as a tool for mass-spectrometry of biological objects, aerosols, quantum dots, etc. or for studying the medium.

Here we report the dependence of the shape of ZC orbits on the value of nonlinear friction is considered. An experimental assembly was created for studying the motion of the particles in nonlinear medium. This set-up consists of standard Paul ion trap with two endcape and one toroidal electrodes. The endcape electrodes are grounded and an AC of up to 6 kV is supplied to the toroidal one. The orbits were shot using a USB camera. A Nd:YAG laser with a radiation power of 100 mW or UV-diode were used to observe the motion of trapped particles.
Figure 1. Extended orbits of a) CdSe/ZnS (core/shell) quantum dots. The quantum dot illuminated by UV-diode what results in QD luminescence; b) lycopodium clavatum. The image is green due to scattering of 532 nm laser radiation by the particle.

Fig. 1 shows ZC-orbits of quantum dots (QD) and lycopodium clavatum pollen. It can be seen that trajectory of QD is rounded and lycopodium clavatum has angulous trajectory. The paths of these objects are different due to distinct values of nonlinear friction coefficient. Nonlinear friction depends on a morphology of the particle, its size and surface undulation. For a spherical particle, the nonlinear friction primarily is dictated by radius of the particle what allows to make relative size measurements using observations of particle trajectories.

The proposed method is not best possible and requires further research. With an improvement of the methodology for observing particle dynamics, it is possible to increase the accuracy of determining the size, as well as to measure the other characteristics of localized objects using unique paths of the charged particles.

References

Complexes of quantum dots and azo-dye molecules for sensor applications

K. I. Annas, A. Dubavik, A. O. Orlova

ITMO University, St. Petersburg, Russia

tyndall64@gmail.com

Quantum dots (QDs) are spherical semiconductor nanocrystals. QDs based hybrid structures are widely used now as highly sensitive sensors for as luminescence sensors to identify the concentration of metal ions in probe or pH-level in living cells owing to their perfect tunable optical properties.

An analyte concentration in sensors based on luminescent QDs is conventionally monitored by the QDs' PL intensity. Contrastingly, we evaluate the change in the analyte concentration by an increase of the initially quenched PL because of efficient intracomplex Förster Resonance Energy Transfer (FRET) in QD/azo-dye complexes. This approach ensures an order of magnitude higher sensitivity of analyte detection. The azo-dye molecule, 1,2-pyridylazo-2-naphthol (PAN), can form chelate complex with zinc atom on the surface of CdSe/ZnS QDs. PL of CdSe/ZnS QDs can be completely quenched by FRET in QD/PAN complexes. We have demonstrated that PAN molecule can desorb from the QD surface leading to QD PL recovery in the presence of an analyte, which has high affinity to PAN. Using porous polyethylene terephthalate (PET) track membranes for analyte pre-concentration is a potential way of detection of extremely low ion concentration.

Our five-year intensive study of photophysical properties of the complexes with different architecture in different media has shown that the desorption of PAN molecules is accompanied by the appearance of local tension in QDs’ lattice, thus giving birth to traps that could become acceptors of electrons or holes. Therefore, sensor properties of such hybrid structures deteriorate, and complexes based on CdSe/ZnS QDs and PAN molecules tend to be useless in real sensor applications.

Here we suggest a route to overcome the limitation associated with trap-states. We demonstrate that replacement of CdSe/ZnS QDs by ZnS QDs
doped by magnesium ions makes QD luminescence insensitive to new nonradiative channels in the QD/PAN complexes due to fast transfer of photoexcitation energy from ZnS matrix to magnesium ions in QDs. This approach opens the way to full potential of QD/PAN complexes in detection of extremely low ion concentration.

References

The theory of holographic recording in photopolymer materials is of a high interest for last decades. Firstly, presented by Zhao\(^1\) and followed by Sheridan\(^2\), it described mass transfer process in terms of self-diffusion of one component (monomer) based on Fick’s laws. Such depiction operates with the effective diffusion coefficient which in common case depends on the component environment, what makes the theory almost useless for predicting the hologram parameters. The second generation of the theory was proposed by Karpov\(^3\), and operates with the so-called interdiffusion coefficient, which does not depend on the components environment. Besides that, it was concluded that for the significant diffusion of a certain component, the other component counterflow has to be existed. Recently, a generalized theory considering multicomponent diffusion was proposed.\(^4\) In this work, we contradict the above theories and propose alternative depiction of multicomponent diffusion processes, directly following from the laws of thermodynamics.\(^5\)

The Karpov’s model for diffusion\(^3\) was derived from Haase’s formulations\(^5\), considering the dependent flow as the one of the immobile component. However, the equation (15) in [3] does not agree with the Fick’s laws and should be correctly rewritten in the form of:

$$j_{M1} = -j_{M2} = -D_1(M_{1,2}) \nabla M_1 \frac{\nabla M_1}{\nabla M_1 + \nabla M_2} + D_2(M_{1,2}) \nabla M_2 \frac{\nabla M_2}{\nabla M_1 + \nabla M_2},$$

(1)

where normalizing coefficients $\frac{\nabla M_{1,2}}{\nabla M_1 + \nabla M_2}$ appear from the exact formulations in [5] and assure the agreement with the Fick’s laws.

Following the Karpov’s derivations, the equation (16) in [3] transforms to:
\[
\frac{D_1}{D_2} = \frac{M_2^2}{M_1^2},
\]

and the equation (17) transforms to:

\[
j_{M_1} = -j_{M_2} = D_0 \left( -M_2 \nabla M_1 \frac{M_2 \nabla M_1}{\nabla M_1 + \nabla M_2} + M_1 \nabla M_2 \frac{M_1 \nabla M_2}{\nabla M_1 + \nabla M_2} \right),
\]

giving the third-order nonlinearity of the diffusion process instead of the second-order nonlinearity depicted in [3] and [4].

The Obukhovsky theory\(^4\) does not contradict with the Karpov’s formulations\(^3\) but does with the correct derivations above. The reason of this, as we believe, is that the Obukhovsky derives the concept from the representation of equal-size surfaces with no vacancies, what is illegitimately for the common case of particles which differ in size. Besides that, Obukhovsky formulations do not consider the third-party flows in the components flow calculations, contradicting with the Haase’s formulations.

Expansion of the corrected Karpov’s formulations to the multicomponent case gives the following equation for the component flow:

\[
j_i = \sum_{l=1}^{m} \left( (-1)^{1-\delta_{il}} \nabla n_i \frac{\nabla n_i}{\sum_{p=1}^{m} \nabla n_p} \sum_{k=1}^{m} (1 - \delta_{il}) D_{kl} n_k^2 \right),
\]

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References
5. R. Haase, Thermodynamics of Irreversible Processes [Russian translation], Izdo Mir (1967).
Hybrid cellulose-inorganic nanostructures as a basis for “smart” materials

Y. A. Sidunets, C. Tracey, E. F. Krivoshapkina, and P. V. Krivoshapkin

SCAMT Laboratory, ITMO University, Russian Federation

sidunets@scamt-itmo.ru

Today, humanity lives in the era of a rubbish crisis and the growing popularity of green chemistry. People have started thinking more about their impact on the planet and therefore try to decrease environmental pollution.

Hence, in recent years, biopolymer-based nanomaterials, like cellulose nanocrystals, have attracted great research interest because of their very high potential for producing high-value products with low impact on the environment. Moreover, cellulose holds the prime position among other biomaterials. It can be extracted from a wide range of natural resources: sugarcane bagasse pulp, rice husk, wheat straw, wood pulp and many others.

Figure 1. The cellulose nanocrystals/gold nanoparticles hybrid material

The materials based on cellulose nanocrystals have a wide range of applications due to a number of their specific properties. One of the main properties is their high porosity which depends on the morphology of the material.

A humidity sensing material based on the high porous structure of the cellulose nanocrystal and gold nanoparticles was proposed. The starting cellulose nanocrystal solution was modified with gold nanoparticles via hydrothermal synthesis. Then the obtained solution was added with the fluorescent Rhodamine 6G dye and dried to obtain final morphology.
The presence of the water molecules in the material has a great impact on the organic dye properties. It causes the quenching of the dye fluorescence and changes the spectrum form. The humidity sensing was observed by decreasing the fluorescence with increasing water concentration.

References

Photophysics of Titania Nanoparticle/Quantum
Dot Hybrid Structures

E.P.Kolesova\textsuperscript{a}, V.G. Maslov\textsuperscript{a}, A. Dubavik \textsuperscript{a}, Y.K. Gun’ko \textsuperscript{b}, A.O. Orlova\textsuperscript{a}

\textsuperscript{a}ITMO University, Saint-Petersburg, Russia
\textsuperscript{b}Trinity College, Dublin, Ireland

e.p.kolesova@gmail.com

The physics of nanoscale materials is one of the most rapidly developing areas of theoretical and experimental solid state physics. The formation of hybrid structures consisting of several types of nanostructured objects is the main direction of nanotechnology development in recent years. This interest is caused by the possibility to combine the unique properties of the components that make up their composition, which allows the creation of multifunctional systems with unique physical properties. Luminescent quantum dots (QDs) of cadmium selenide are traditional inorganic luminophore with well-studied properties\textsuperscript{1}. Structures based on titanium dioxide (TiO\textsubscript{2}) nanoparticles and QDs can combine the high photocatalytic activity of TiO\textsubscript{2} with the ability of QDs to absorb radiation in a wide spectral range and act as an effective phosphor\textsuperscript{2}. The band structure of QDs and Titania nanoparticles allows for highly efficient photoinduced electron transfer from QDs to TiO\textsubscript{2} nanoparticles, which allows the formation of structures exhibiting activity under both UV and visible radiation\textsuperscript{3}.

Despite the promise of hybrid structures, systems with fully realized potential have not yet been formed. To identify the reasons for the low efficiency of the realized photoinduced electron transfer from QD to Titania nanoparticle, it is necessary to identify relaxation channels of electronic excitation in QDs, which are able to effectively compete with this process. For this purpose, it is necessary to estimate electron transfer efficiency in the formed structures.

In this work, hybrid structures were formed based on three types of quantum dots: core CdSe QDs and core/shell CdSe/ZnS QDs with different shell thickness. The electron transfer efficiency was estimated both from luminescence properties of the donor (QDs) and from photocatalytic
properties of the acceptor (TiO$_2$). Therefore, we have developed a new approach to electron transfer efficiency estimation in TiO$_2$/QDs systems based on measuring ROS generation. We demonstrate that taking into account a multiexponential QDs luminescence decay and inhomogeneity of luminescence quenching of QDs in structures allows correctly estimate electron transfer rate (~10$^{10}$ s$^{-1}$) and efficiency can be increased from 25% to 54% with replacing large CdSe/ZnS QDs with 5.5 nm core size by smaller CdSe QDs with 2.5 core size.

These results made it possible to determine the key parameter limiting the electron transfer efficiency in TiO$_2$/QDs structures. As a possible way to optimize structures properties, we used preirradiation of QDs. It is well known that efficiency of nonradiative processes in QDs can be controlled using so-called QDs photoactivation, i.e. irradiation of QDs surface with light efficiently absorbed by QDs$^4$. We demonstrate that «dark» fraction in QDs ensemble decreased by half due to irradiation of QDs and electron transfer efficiency threefold increased. Our results clearly demonstrate the prospects of Titania nanoparticles/QDs structures as efficient ROS generator under visible light and show that photoinduced processes on the QDs surface can used for optimize structures parameters.

References

2. Y. Li et al. Mechanism of photogenerated reactive oxygen species and correlation with the antibacterial properties of engineered metal-oxide nanoparticles, ACS nano 6, 5164-5173 (2012).
4. C. Carrillo-Carrión, S. Cárdenas, B. M. Simonet, M. Valcárcel, Quantum dots luminescence enhancement due to illumination with UV/Vis light, Chemical Communications 35, 5214-5226 (2009).
Photocatalytic Properties of Thermally Annealed Films of Titanium Butoxide

A.A. Lazareva\textsuperscript{a}, E.P. Kolesova\textsuperscript{a}, M.A. Baranov\textsuperscript{a}, A.O. Orlova\textsuperscript{a}

\textsuperscript{a}ITMO University, Saint-Petersburg, Russia

lazareva.a.a@mail.ru

Currently, to structures based on nanomaterials capable of treating bacterial infections are attracting researchers' close attention. Such structures can be titanium dioxide nanoparticles that are able to generate reactive oxygen species upon absorption of UV radiation\textsuperscript{1}. One of the possible mechanisms of killing bacteria is the oxidative stress caused by interaction of bacteria with reactive oxygen species (ROS) generated by nanoparticles. This fact makes titanium dioxide nanoparticles promising material for antibacterial therapy. There are works in which nanostructured titanium dioxide films were obtained by annealing films from precursors, in particular titanium butoxide\textsuperscript{2}. The formation of films from precursors has several advantages compared to films based on colloidal titanium dioxide nanoparticles. The main one is the ability to form homogeneous nanostructured film.

The purpose of this work is to identify the patterns of ROS generation by a nanostructured film obtained through annealing a titanium butoxide film. The titanium butoxide films were obtained by sequential deposition of precursor onto a dielectric substrate using the Langmuir-Blodgett technology and contained 15 layers of the precursor. We demonstrate the effect of water pH and temperature on the stability of precursors at the water-air interface and show that pH=6 at 15 °C is the optimal condition for formation of titanium butoxide films. Formed films were annealed at a temperature of 500 °C for 30 minutes. An unannealed film formed under identical conditions was used as a reference sample. The efficiency of ROS generation has been studied using the RNO chemical sensor, whose absorption band at 440 nm bleaches due to its interaction with ROS\textsuperscript{3}. As a result of annealing of the precursor film, a nanostructured titanium dioxide film is formed, capable of generating ROS (Fig. 1). At the same time, the bleaching of sensor absorption band was not observed in unannealed samples.
Figure 1. The dependence of optical density of RNO absorption band at 440 nm on radiation (365 nm) dose in samples for annealed (1) and not annealed (2) samples.

Our results clearly demonstrate that nanostructured titanium dioxide films capable of ROS generation was formed because of titanium butoxide film annealing. The analysis of photobleaching rate of RNO due to its interaction with nanostructured titanium dioxide films has shown that ROS generation efficiency by annealed films is comparable to the film formed from colloidal titanium dioxide nanoparticles.

In the future, it is planned to study the influence of annealing conditions on photocatalytic properties of nanostructured titanium dioxide films.

References
Optical properties of hybrid structure based on silver nanoparticles and carbon thin films

M. M. Abboud\textsuperscript{a,b}, E. A. Konshina\textsuperscript{a}, D. P. Shcherbinin\textsuperscript{a}, V. V. Zakharov\textsuperscript{a}
\textsuperscript{a}ITMO University, Saint-Petersburg, Russia
\textsuperscript{b}Mansoura University, Mansoura, Egypt
m.mostafa.h88@gmail.com

In the present study, optical properties of thin-solids hybrid structures consisted of silver nanogranulated film deposited on amorphous hydrogenated carbon (a-C:H) have been investigated. Gravimetric thickness of silver film varied as 2, 4 and 10 nm. Amorphous hydrogenated carbon films with narrow (0.4 eV) and wide (2.7 eV) optical gap were used. The blue shift of plasmonic peak have been observed in the hybrid structures with the enhancement of a-C:H optical gap regardless gravimetric thickness of silver films. The maximum value of blue shift (150 nm) compared to the carbonless samples has been observed in the hybrid structures with wide-gap carbon. In the hybrid structures with 4 and 10 nm silver gravimetric thickness weak short wave peak was excited in addition to main peak. The appearance of short-wave peak may be due to quadrupole moment excitation. It has been shown, that the efficiency of interaction between $\pi$-electrons of a-C:H and localized surface plasmons of silver NPs depend on both - silver film morphology and structure features of a-C:H.

Photoluminescence (PL) of a-C:H in hybrid structures with silver NPs has been investigated. PL intensity depends on both the gravimetric film thickness and the optical gap of amorphous carbon. PL quenching have been observed in the hybrid structures consisted of wide-gap carbon and 2 as well as 4 nm silver film. In the same time two-fold enhancement of wide-gap a-C:H PL have been achieved in hybrid structures with 10 nm silver thickness as a result resonant exciton-plasmon interaction. The same silver film led to 19 times PL enhancement of narrow gap a-C:H. The higher enhancement factor if
bigger nanoparticles can be explained as a deeper penetration of the evanescent plasmon wave into the a-C:H volume. The structure of narrow gap a-C:H can be characterized by bigger π-bonded cluster and higher density of dangling bonds on a-C:H surface. Such dangling bond can be serving as electron traps provides path for nonradiative relaxation of photo excited electron-hole pairs. The passivation of dangling bonds by excited electrons from plasmonic silver granules contribute to a-C:H PL enhancement.

**Figure 1.** The photoluminescence spectra of a wide-gap (a) and narrow-gap (b) a-C:H thin-film in hybrid structures with the granulated silver films with different thickness at the excitation wavelengths of 488 nm
Chirality is a fundamental property of the natural world. “Chiral” refers to those objects that cannot be superimposed on their mirror image.

Chiral objects exist not only among molecular objects, but also among nanocrystals. Chiral nanocrystals are currently being intensively investigated, and are presumed to have a significant effect on the development of nanotoxicology and nano-bio-technology. In particular, it is expected that chiral nanocrystals will have different biocompatibility compared to their achiral analogs, that will allow such nanocrystals to interact with biosystems using the chiral molecular recognition mechanism. We have reported an investigation of optical activity which was photochemically induced by illumination of quantum dots with circularly polarized light; the photoinduced circular dichroism was quantitatively estimated, and it was shown that the photoinduced chemical reaction proceeds selectively, depending on the handedness of circularly polarized light.

The aim of this research is an extension of the class of objects in which the effect of photochemically induced circular dichroism could be observed from quantum dots to quantum rods and from liquid solutions to solid layers.

In this work, we used dry samples of CdSe/ZnS quantum rods (diameter 3nm, lengths 35 nm) on a glass substrate, as well as CdSe/CdS Dot-in-Rods (diameter 5 nm, 35 nm lengths)dissolved in chloroform. Colloidal solutions of nanocrystals were dropped to a glass substrate to complete evaporation of the solvent from the glass surface. The sample was dropped until the transparent window was uniformly filled with nanocrystals. We used a LED with a wavelength of 625 nm (bandwidth 59 nm) for quantum rods and LED with a wavelength 460 nm (bandwidth 55 nm) for Dot-in-Rods. The study of photoinduced optical activity was carried out using spectroscopy of circular dichroism (CD) JASCO J-1500. The change in optical density ($\delta D$) caused by
photoreaction reached about 0.1 in the case of Dot-in-rods and 0.05 in the case of rods.

We have shown that an optically active ensemble of nanocrystals can be produced as a result of photochemical reaction induced by circularly polarized light.

The general dissymmetry factor for samples of quantum dots with photochemically induced circular dichroism is 3-5 times lower in magnitude to the dissymmetry factor of intrinsically chiral quantum dots separated by enantioselective phase transfer.

Table 1. The value of the dissymmetry factor (g1) of the CdSe/ZnS nanorods for the first exciton transition

<table>
<thead>
<tr>
<th>Wavelength of CD peak (nm)</th>
<th>The sign of the difference in the CD curves (L-R)</th>
<th>The value of CD (L-R), (mdeg)</th>
<th>The value of optical density (D)</th>
<th>The value of the dissymmetry factor (g1)</th>
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</thead>
<tbody>
<tr>
<td>610 (Rods)</td>
<td>-</td>
<td>0.33</td>
<td>0.814</td>
<td>1.2·10⁻⁵</td>
</tr>
<tr>
<td>466 (Dot-in-Rods)</td>
<td>-</td>
<td>0.25</td>
<td>0.484</td>
<td>1.5·10⁻⁵</td>
</tr>
</tbody>
</table>

References

Photoactivated luminescence of quantum nanoplatelets

V. N. Smelov, V. G. Maslov

ITMO University, St. Petersburg, Russia

smelov.vn@mail.ru

Colloidal semiconductor nanoplatelets (NPs) are nanocrystals with a flat geometry. These crystals can have large lateral sizes (tens of nanometers), but they differ in small thickness of several nanometers (usually 4-6 monolayers). Compared to quantum dots (QDs), NPs have several important advantages. First, in the synthesis of NPs, it is possible to control the thickness at the atomic level; as a result, narrower bands in the absorption and luminescence spectra are achieved. Secondly, the plane surface geometry allows to consider NPs as substrates for the growth of other nanostructures.

Many studies report the possibility of increasing the luminescence intensity of quantum nanocrystals when irradiated with light. This enhancement of luminescence is commonly called “photoactivation”. This phenomenon was first described by Cordero et al. in 2000, who described the effects of increased luminescence in TOP / TOPO-CdSe QDs. Since then, a lot of researches has been done in this area, but the exact mechanism of photoactivation is still unknown. This uncertainty is due to the fact that the studies were carried out under different conditions: the nanocrystals were synthesized by different methods, the intensities of the irradiating light were different, or were not indicated at all in the articles, during irradiation the nanocrystals were placed in different media. Due to this, various explanations of the reasons for photoactivation were given.

Over 20 years since the start of photoactivation studies, along with the activation of other nanocrystals (QD, nanorods), photoactivation of NPs has also been studied. However, the true reasons and features of the photoactivation phenomenon for NPs remain not fully established.

In this work, we studied the photoactivation of CdSe NPs under different conditions of irradiation and measurements. The characteristic results obtained for the two types of experimental setup are shown in Fig. 1.
Fig. 1 (a), the black curve corresponds to the change in the luminescence intensity of the sample subjected to constant irradiation (intensity of irradiation is about 5 mW/cm², the maximum intensity of the irradiating light is at 465 nm.) and isolated from the air by a dense lid. Red curve describes the results of similar measurements with the same sample, but which has direct contact with the environment. This study shows that the atmosphere in which the sample is located has a decisive influence on the photoactivation process. Figure 1 (b) shows the dynamics of the dark evolution of irradiated samples isolated from air, i.e. the intensity with which a sample can emit upon excitation, depending on the time elapsed since activation. The purple arrows pointing up and down show respectively the moments of turning on and off the light irradiating the sample. From this experiment it follows that when we turn off the irradiation of the sample, the NPs do not retain the obtained changes for a long time, i.e. relaxation processes occur in the NP.

![Graph (a)](image1a.png)

![Graph (b)](image1b.png)

**Figure 1.** Change in luminescence during photoactivation of NP

The following conclusions can be done from the described experiments. Firstly, in the presence of oxygen, the effect of light on NPs does not lead to an increase, but to a decrease in the luminescence intensity. Secondly, the activation effect is reversible: after the end of irradiation of the NPs, they return to a state close to the initial one, and can be activated again. We also note that the process of activation of luminescence of NPs is rather fast (less than 5 minutes). Presumably, the processes of activation of luminescence and reverse relaxation are associated with charge transfer between the volume of the NPs and defective states.
Photocatalytic Heterostructures Based on TiO$_2$ Nanoparticles and Graphitic Carbon Nitride Nanosheets

A. A. Makovektkaya$^a$, E. P. Kolesova$^a$, M. Mathew$^b$, Ch. S. Rout$^b$, and A. O. Orlova$^a$

$^a$ITMO University, St. Petersburg, Russia
$^b$Jain University, Bangalore, India

anastasiya.makovectkaya@mail.ru

Creation and research of new antibacterial systems have great importance because of the problem of bacterial resistance to antibiotics. Titanium dioxide nanoparticles (TiO$_2$ NPs) are widely used as a base of antibacterial systems due to their significantly high photocatalytic activity, chemical stability, non-toxicity and cheapness. The of TiO$_2$ NPs ability to generate reactive oxygen species (ROS) only under the UV light because of their band gap energy (3.2 eV) restricts the application of TiO$_2$ in living systems because of damage to cells and tissues by UV light. Respectively, many studies aim at creation of antibacterial systems based on TiO$_2$ NPs, which will be active in the visible spectral range$^{1,2}$.

The attractive material, which can help to achieve the goal, is an organic semiconductor graphene-like carbon nitride (g-$C_3N_4$)$^3$. This nontoxic material can be obtained by simple and low-cost synthesis. The bandgap energy of g-$C_3N_4$ nanosheets (NS) within 2.7-2.8 eV is appropriate for electron transfer from g-$C_3N_4$ to TiO$_2$ NPs. g-$C_3N_4$ nanosheets are also able to generate ROS$^{3,4}$, and all these facts make g-$C_3N_4$ and systems based on such nanosheets interesting objects for studying photocatalytic properties.

In this work the ROS generation by TiO$_2$ NPs/g-$C_3N_4$ NS heterostructures with different TiO$_2$ NPs to g-$C_3N_4$ NS ratio (from 3:1 to 3:4) under UV and visible light (405 nm) has been studied. ROS generation by TiO$_2$ NPs/g-$C_3N_4$ NS heterostructures has been examined by bleaching of p-Nitrosodimethylaniline (RNO) molecules used as chemical sensor on superoxide and hydroxyl radicals. All heterostructures have shown higher ROS generation efficiency than pure TiO$_2$ NPs and g-$C_3N_4$ NS that confirms
synergy effect. The analysis of sensor bleaching rate has shown that ROS generation efficiency of the samples drastically depends on component ratio in the heterostructures. The strongest effect in the samples exposed by UV and visible light has been observed at TiO$_2$ NPs:g-C$_3$N$_4$ NS ratio equal to 3:2.

Our results clearly demonstrate that interaction of TiO$_2$ NPs and g-C$_3$N$_4$ NS in heterostructures leads to ROS generation enhancement due to some synergy effect and finding of optimal component ratio is needed to achieve the strongest photocatalytic effect.

**References**

Light-induced ion fluxes for self-assembly and biomimetic information processing

N. V. Ryzhkov and E.V. Skorb
ITMO University, Saint Petersburg, Russia
ryzhkov@scamt-itmo.ru

Due to stable and robust photoactivity TiO$_2$ is widely used in design of solar cells and photocatalyst for environmental purposes. It has recently been shown that under focused irradiation, pH gradient is generated on the surface of anodized Ti/TiO$_2$ in water solutions. The photocatalytic activity of TiO$_2$ is based on photogenerated electron-hole pairs. In case of Ti/TiO$_2$ under the field of the Schottky junction, holes reach the semiconductor–solution interface and react with surrounding water media to form proton flux.

Figure 1. a) Photoelectrochemical decomposition of water on the surface of photoexcited TiO$_2$, due to n-type conductivity of nanostructured Ti/TiO$_2$ photoexcited holes are captured by surface states and water splitting with proton release occurs at TiO$_2$-solution interface inside irradiated spot whereas electrons being a major charge carriers are transferred to bulk titanium, b) irradiated by UV 365 nm spot on the surface of Ti/TiO$_2$, c) pH map of irradiated Ti/TiO$_2$

The protons formed at the semiconductor-water solution interface as a result of the photocatalytic decomposition of water trigger the propagating 'pH wave' and create the 'proton field' like the fields of morphogens.
Morphogen is a substance producing in a certain part of the developing organism in a certain concentration, propagating and acting on cells, determining their further path of development. Morphogen gradients determine the complex morphology of living tissue. Controlled by the proton gradient, local self-assembly on the surface of semiconductors is of great interest for surface functionalization and tissue engineering, as well as in the development of biosensors and ‘smart’ materials. In this work, we propose a new strategy for the formation of supramolecular peptide hydrogels of films by generating morphogen on a photosensitive substrate upon irradiation with the simultaneous presence of all reagents in solution.

Arising from foregoing, we propose consideration of ion fluxes in solution as information transducers, which give a signal to state switching in solution chemistry\(^2\) and even able to perform simple logic operations\(^3\).

References


Bifunctional deoxyribozymes based nanodevice for cancer theranostics

E. A. Goncharova, A. M. Savin
ITMO University, Saint Petersburg, Russian Federation
katerina.burmina@gmail.com

Theranostic approaches based on the simultaneous diagnostics and therapy provide a transition from traditional to personalized medicine. A number of approaches based on nanomaterials and self-organizing DNA nanostructures have been proposed for the development of theranostic agents. Deoxyribozymes (Dz) are synthetic DNA molecules that catalyse chemical reactions of the phosphodiester bond cleavage between nucleotides in the presence of bivalent metal ions. Dz have the ability to cleave specific RNA sequences, which is one of the methods of cancer gene therapy. Moreover, binary Dz can also detect specific RNA or DNA fragments by fluorescent assay. In this approach, two DNA strands (binary Dz — Dza and Dzb) bind the target RNA and cleave the DNA sequence labelled with a fluorophore and quencher (F_sub). F_sub cleavage occurs only in the presence of the target RNA sequence and leads to the generation of a fluorescent signal. However, both of these approaches have limited effectiveness when working with long RNA sequences.

In our study, we combined detection and cleavage of RNA in one theranostic DNA nanodevice (TDN). An important feature of the proposed TDN is the presence of several short additional DNA chains, which increase the affinity for the target RNA and promote the unwinding of a stable secondary structure of the target RNA for effective theranostic work. As a model RNA sequence, we chose the oncological marker KRAS, which is involved in the regulation of cell growth and proliferation in many oncological diseases.

To demonstrate the therapeutic function of TDN, we conducted an experiment in which an RNA marker labeled with FAM (KRas-58F) was incubated in a buffer containing 10 mM MgCl₂, 150 mM KCl, 50 mM NaCl, 50 mM HEPES pH 7.4, in the presence of TDN during 15, 30, 60, 120 and 180
minutes at a temperature of 37 °C. Next, we performed 17.5% denaturing polyacrylamide gel electrophoresis with an assessment of cleavage of KRas-58F.

Further, in order to evaluate the diagnostic function of TDN, we determined the detection limit of the target KRas-58 RNA, not labeled with FAM, in a solution containing buffer (10 mM MgCl2, 50 mM HEPES, pH 7.4, 50 mM NaCl, 150 mM KCl, 1% DMSO, 0.03% Triton-X100), TDN, and F_sub. The concentration of KRas-58 was 0.25 nM, 0.5 nM, 1 nM, 2 nM, 5 nM, the incubation lasted for 180 minutes at a temperature of 37 °C. The fluorescence of the solutions was measured using an Agilent Cary Eclipse spectrofluorimeter.

The study revealed that the maximum percentage of cleavage after 180 minutes was 57%, the data were obtained using Adobe Photoshop quantitate tool. The detection limit of the KRas-58 RNA marker was also determined as 0.5 nM. It was found that the detection and cleavage parts work equally efficiently and do not interfere with each other.

In conclusion, we have developed the DNA nanodevice that can simultaneously report the presence of the RNA marker in solution by fluorescent signal increase and at the same time destroy the RNA marker by cleavage. Bifunctionality was achieved by combining an RNA-cleaving Dz (therapeutic function) and an RNA-detecting binary Dz sensor (diagnostic function). The proposed design may be the starting point in the development of theranostic nanodevices in RNA therapy and diagnostics.

References
Visual detection of central nervous system pathogens

D.A.Gorbenko\textsuperscript{a,b}, E.Goncharova\textsuperscript{b}, D. Nedorezova\textsuperscript{b}

\textsuperscript{a}ITMO University, St.Petersburg, Russia
\textsuperscript{b}Ioffe Institute, Russian Academy of Sciences, St. Petersburg, Russia

gorbenko@scamt-itmo.ru

Various methods can be used for detection of single-stranded DNA or RNA: fluorescent TaqMan probes, molecular beacon probes\textsuperscript{1}. Actually, their disadvantages are low selectivity and frequent false-positive results. In this research, we propose a diagnostic method based on hybridizing DNA constructions containing guanine quadruplexes (G-4). G-4 are the structures of guanine tetrads supported by Hoogsteen bonds. Main advantage of G-4 is the ability to bind to hemin with formation of a peroxidase, which mimics DNAzymes and RNAzymes\textsuperscript{2} activity. As a detection agent, a G-4 probe is used divided into 2 parts (G-4 split) and connected through a spacer (triethylene glycol) to an oligonucleotide sequence that recognizes the target single-stranded DNA or RNA (analyte). In the absence of analyte, 2 parts of G-4 exist mainly in dissociated form. When 2 parts of G-4 are added to the analyte solution, they assemble into a complex and acquire peroxidase activity. Active peroxidase catalyzes the oxidation of a colorless substrate to a colored product, which can be detected both visually and spectrophotometrically. This diagnostic method is financially profitable and highly accurate, what makes it a great diagnostic tool.

In this research, we accomplished multiplex diagnostics of several pathogens of central nervous system - E. coli, S. pneumoniae, and N. meningitidis. Each pathogen sensor consisted of 2 split oligonucleotides – m and f chains – that form G-4 in the presence of the target single-stranded DNA analyte. We performed multiplex detection of 3 synthetic analytes by mixing 1 \( \mu \)M of f-chains of E. coli, S. pneumoniae and N. meningitides sensors with 1 \( \mu \)M of different m-chains in the presence of 1 \( \mu \)M of various DNA analytes in the detection buffer (50 mM HEPES (pH 7.4), 50 mM MgCl\textsubscript{2}, 20 mM KCl, 120 mM NaCl, 0.03% Triton X-100, 1% DMSO). To conduct the reaction, 1 mM
H₂O₂, 1 mM diaminobenzidine hydrochloride (DAB) and 1 μM hemin were added to the oligonucleotide mixture. As a result, multiplex detection of synthetic analytes was performed: in the presence of target DNA the samples produced a visual reaction with an optical density (was measured at 500 nm using Implen NanoPhotometer 80) change in 10 (for E. coli) and 20 times (for S. pneumoniae, N. meningitidis) higher compared with negative control (Fig. 1). The coloration was observed only in samples where the DNA and m-chain matched (samples 1, 5 and 9).

![Image of multiplex detection](image)

**Figure 1.** Multiplex detection of synthetic DNAs. Samples 1–3 contain the m-chain of the E. coli sensor, 4–6 — the m-chain of the S. pneumoniae sensor, 7–9 — the m-chain of the N. meningitidis sensor. Samples 1, 4, 7 contain synthetic E. coli DNA, 2, 5, 8 - S. pneumoniae DNA, 3, 6, 9 - N. meningitidis DNA.

Thus, as a result of the research, 3 biosensors based on binary G-4 were constructed as tool for rapid multiplex DNA detection. These biosensors have a high potential for visual detection. The next step in this research is to analyze DNA obtained from human samples by polymerase chain reaction to screen pathogens of central nervous system.

**References**

Over the last decades, the optical properties of metallic nanoparticles have been exploited for light manipulation, ultrasensitive spectroscopy and sensorics\textsuperscript{1}. Many of these applications are underpinned by the fact that the optical absorption of organic molecules on the surface of nanoparticles is enhanced\textsuperscript{2}. However, in such studies the dye concentration is often large to maximize interactions. So dye–dye interactions cannot therefore be neglected and are expected to induce resonance shifts of the dye layer independently of any effects of nanoparticles. In fact, many studies specifically work with J-aggregates rather than isolated monomers\textsuperscript{3,4}.

The overlapping of plasmon resonances of nanoparticles and the absorption band of a molecular layer of the cyanine homologues was studied for thin film. The nanoparticles in form of the island film of gold or silver were obtained by thermal vacuum deposition. The homologous series of cyanine dyes differing in the length of the conjugation chain (pseudo-, mono- and dicarbocyanines) and the absorption maximum was chosen as organic molecules. Hybrid films consisting of monomers and aggregates were obtained by spin-coating of dye solution on island films.

The absorption of dicarbocyanine dye in the presence of nanoparticles for both metals was increased by several times. However, enhanced absorption of a shorter wavelength dyes (monocarbo- and pseudoisocyanine) is observed only for the Ag island films. This is explained by the longer-wave position of the plasmon resonance of gold nanoparticles with respect to the dye absorption, which leads to the decrease of plasmon near fields. The dip in the absorption spectrum of the hybrid film at a wavelength corresponding to the maximum of the J-aggregate band is observed for pseudoisocyanine coated on nanoparticles of both metals. The presence of the transparency is explained
by the strong coupling of the exciton transition in the J-aggregate with the plasmon resonance of nanoparticles.

References
Influence of the ligand chain length on the optical properties of QD-Au NPs colloidal complex

I.A. Arefina\textsuperscript{a}, T.K. Kormilina\textsuperscript{a,c}, E.A. Stepanidenko\textsuperscript{a}, D.A. Kurshanov\textsuperscript{a}, S.A. Cherevkov\textsuperscript{a}, A. Dubavik\textsuperscript{a}, A.P. Litvin\textsuperscript{a}, A.V. Baranov\textsuperscript{a}, E.V. Ushakova\textsuperscript{a,b} and A.V. Fedorov\textsuperscript{a}

\textsuperscript{a} Center of Information Optical Technologies, ITMO University, Saint Petersburg, Russia
\textsuperscript{b} Department of Materials Science and Engineering, City University of Hong Kong, Hong Kong SAR, PR China
\textsuperscript{c} Friedrich-Alexander Universität Erlangen-Nürnberg, Erlangen, Germany

ela.ushakova@itmo.ru

Among hybrid systems, there is a special class of heterostructures formed from semiconductor nanocrystals and noble metal nanoparticles, which can be used in the development of multicomponent materials for the photonic applications, biological imaging, and solar cell technologies. For successful implementation in these areas, it is important to understand the factors that influence the formation processes, morphology, and characteristics of complexes. The aim of this work was to determine the optical parameters of semiconductor quantum dot (QD) complexes - gold nanoparticles (GNPs) covalently bonded by ligand molecules of mercaptocarboxylic acids with a different chain length.

Colloidal Au NPs were synthesized following the procedure\textsuperscript{1}. Alloyed CdZnSe/ZnS quantum dots were used as the semiconductor nanocrystals colloidal; QDs were synthesized by the organo-metallic method\textsuperscript{2}. Due to a different molar ratio of Cd and Zn, QDs with luminescence in the green (QD\textsubscript{1}) and red (QD\textsubscript{2}) spectral regions were obtained. To synthesize GNPs-QD complexes we followed the procedure previously\textsuperscript{3}. As ligand molecules a 3-mercaptobenzoic acid (3-MBA), a 6-mercaptophexanoic acid (6-MHA), and a 11-mercaptopoundecanoic acid (11-MUA) with different chain lengths (0.7-1.4 nm) were used.

Since the absorption spectra of the QD-GNP complexes are additive to the initial solutions, we inferred that the binding of nanoparticles into complexes does not change their chemical composition. The average PL
lifetimes are almost independent of the distance between nanoparticles in the complexes. This indicates that the interaction between QDs and GNPs does not influence the rate of radiative recombination of QDs.

Figure 1. Dependence of PL enhancement (a) and PL lifetime (b) from the ligand chain length

For all series of samples, greater PL enhancement is observed for a smaller ligand chain (Fig. 1). For complexes made with QD1, an enhancement of up to 3.1 times is observed; this is caused by resonance of both absorption and PL spectra with plasmon of GNPs.

The obtained results improve the understanding of processes occurred in multicomponent complexes. Precise control over these factors is necessary for the successful implementation of new materials in modern optoelectronic and biochemical systems.

References
Chromatographic separation of dye molecules due to their selective photo-excitation

G.G. Anchutkin\textsuperscript{a}, S.A. Pliastsov\textsuperscript{a}, G.P. Miroshnichenko\textsuperscript{a}, and
I.K. Meshkovskii\textsuperscript{a}
\textsuperscript{a}ITMO University, Saint Petersburg, Russia
gord.gl@yandex.ru

There is a global problem of water quality, which will lead to the development of technologies for its purification. One of the pollutants are, for example, enterprise textile, food, and the dyeing industry because of their content of organic dyes\textsuperscript{1}. Techniques for removing dyes from aquatic environment are widely studied\textsuperscript{2,3}. In the present work, a hypothesis of the possibility of dye separation using the selective excitation of molecules by optical radiation\textsuperscript{4} was investigated. After absorbing energy, the molecules are excited in singlet state, then it is able transfer into a triplet states in course of intercombination conversion process. Molecules in the triplet state have essentially other polarizability and dipole moment values. Adsorption activity of excited molecules increases.

We used an experimental setup based on usual chromatographic column (with silica gel 60-200 μm size) and an irradiating laser (with a radiation power of up to 3 W). Mixture of organic dyes Rhodamine 6G and Oxazine 1 perchlorate was used, see Fig. 1a. The molecules of Rh6G dye effectively absorb laser radiation (532 nm) and then transit into the triplet state, the molecules actively interact with surface of the silica gel stationary phase. This process slows down the diffusion rate of Rh6G molecules through the column. Both dyes were detected with use of a spectrofluorimeter.

Experimental studies of the 532 nm (up to 5.5 W/cm\textsuperscript{2} laser radiation) effect on the diffusion rate of the Rh6G and Oxaz solution through the column have been carried out, see Fig. 1b. It is observed that the peak of Rh6G shifts by 30 min, diffusion rate of Oxaz remained practically unchanged.

The theoretical dependence was proposed that describes the diffusion rate of Rhodamine 6G depending on the pumping rate. The character of the change in the dye diffusion rate is demonstrated, based on the parameters of quantum transitions from the ground singlet state to the excited state, and to
the triplet state. The experimental data obtained in course of present study are in qualitative agreement with the model.

**Figure 1.** Absorption spectra of the dyes mixture: Rh6G and Oxaz (a). Diffusion of Rh6G through the chromatographic column before and during laser irradiation at 2.5 W/cm² and 5.5 W/cm² laser power density (b).

In course of the present work, it was shown that after selective photoexcitation of Rhodamine 6G molecules and their transition into triplet state, the diffusion rate decreases by 40% compared with molecules in the ground state. We hope to use the theoretical model to study the diffusion of other organic molecules in further research. The presented data on the slowing down of the diffusion rate of dyes in the triplet state through porous media can be used to study new methods of chromatographic separation of substances.

**References**

Nanodiamond-tetracarboxyphenylporphyrin complexes: characteristics, detection and visualization in human cells

A. G. Masyutina, M. V. Erokhinaa, E. K. Tarasova, G. E. Onishchenkoa,
V. A. Lapinab, T. A. Pavichb, Y. B. Tsaplevc, P. P. Zakc and A. V. Trofimovc

aLomonosov Moscow State University, Moscow, Russian federation
bB.I. Stepanov Institute of Physics, National Academy of Sciences of the Republic of Belarus, Minsk, Belarus
cEmanuel Institute of Biochemical Physics, Russian Academy of Sciences, Moscow, Russian federation

imber.acidis@gmail.com

One of the most promising variants of targeted drug delivery is the use of nanoparticles as drug-carriers. In the stage of pre-clinical studies, the main goal is to visualize these particles, to control their destination and accumulation in living organism. Thus, it is convenient to use materials with controlled optical properties. Diamond nanoparticles (ND) are of considerable interest, due to their small size and labile surface. ND surface may be functionalized in various ways, which allows using them as a drug-carrier or conjugate them with fluorochrome for visualization. Our work presents model studies of complexes of nanodiamonds with tetracarboxyphenylporphyrin (TCPP) as a fluorescent agent. The aim of the present study was to characterize the studied nanoparticles, detect them in human macrophages and test their fluorescent properties after their internalization by cells.

Synthesis of nanodiamond-TCPP (ND-TCPP) complexes was carried out using ultrafine synthetic diamonds brands "UDA-SP" NP ZAO "Sinta" (Minsk, Belarus). To characterize these nanodiamonds and their intracellular localization, the methods of conventional and analytical transmission electron microscopy, as well as laser scanning confocal microscopy (LSCM, excitation spectrum 400 nm, and emission spectrum – 655 nm) were used.

In an aqueous suspension, NA-TCPP nanoparticles form aggregates up to 200 nm in size. Individual nanoparticles (4-7 nm) have polygonal shape.
High-resolution transmission electron microscopy showed the crystal lattice bands and electron diffraction patterns, which demonstrates the crystallinity of nanodiamonds and make it possible to further identify them in human cells.

THP-1 is a human monocytic cell line derived from an acute monocytic leukemia patient and used for modeling phagocytosis processes. The addition of phorbol ester at a final concentration of 100 nM induces macrophage differentiation, cells attach to the substrate, spread and gain macrophage phenotype. On the third day of differentiation, a suspension of nanodiamonds (50 μg/ml) was added to the culture medium for: 1) 30 min and 2) 24 hours. After incubation, the cells were washed and fixed for further research.

Using LSCM, we have shown that after a 30-minute incubation, fluorescent nanoparticles were detected mainly at the periphery of the cells. 24 hours of incubation lead to a greater accumulation of nanodiamonds in cytoplasm, while the absorbed clusters were detected mainly around nucleus. Still, after 24 hours, ND-TCPP retain their fluorescent properties.

Ultrastructural analysis did not reveal any pathological changes in cells. The cells formed numerous 1-2 μm long protrusions to actively absorb aggregates of nanodiamond complexes. In cytoplasm, ND-TCPP are detected in numerous endosomes ranging in size from 200 nm to 3 μm. The crystalline nature of electron-dense inclusions in the endosomes is confirmed by the electron diffraction pattern of ND-TCPP.

Thus, the ND-TCPP complex retains its crystalline structure and fluorescent properties when absorbed by cells. This allows us to further visualize these nanoparticles using methods of both electron microscopy and LSCM. The intense absorption of the nanocomplexes by cells, and their effective visualization suggests that such complexes can be used to transfer therapeutic agents into cells, as well as to study the localization of such complexes in intracellular compartments.

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IR luminescence parameters control in multifunctional associates based on Indocyanine Green and Ag$_2$S quantum dots for theranostics in oncology

T.S. Kondratenko$^a$, M.S. Smirnov$^a$, O.V. Ovchinnikov$^a$, I.G. Grevtseva$^a$

$^a$Voronezh State University, Voronezh, Russia

tamara-shatskikh@rambler.ru

The development of sustainable multifunctional complexes for theranostics of oncological pathologies is actuality. Currently, Indocyanine Green (ICG) is a promising material in this field. The formation of hybrid associates with colloidal quantum dots (QDs) is one of the promising methods for improving the luminescent parameters of dyes, especially the intensity and color contrast of luminescence, which is determined by the difference in the wavelengths of its excitation and detection. In this work, we consider the spectral features of the IR luminescence sensitization in hybrid associates of colloidal Ag$_2$S quantum dots passivated with thioglycolic acid molecules (Ag$_2$S/TGA QDs) with average sizes of 2.2-3.7 nm and ICG monomers (J-aggregates).

Ag$_2$S/TGA QDs were prepared with using the synthesis technique$^1$. The obtained Ag$_2$S quantum dots were conjugated with ICG monomers (J-aggregates) by mixing an aqueous dye solution with colloidal Ag$_2$S/TGA QDs solution. The dye concentration in mixture with QDs was determined corresponding to relation of $10^{-4}$-$10^{-2}$ mole ICG / mole QDs contained in this volume of the colloidal solution (further m.f.). A dye solution with a predominant monomers fraction was obtained by sequential dilution of a freshly prepared ICG aqueous solution to concentrations of $10^{-5}$-$10^{-6}$ mole/dm$^3$. Dye J-aggregates were preliminarily obtained by keeping an aqueous ICG solution at a concentration of $10^{-3}$ mol / L at a temperature of 65-67$^0$C for 32 hours. Comparison samples were obtained from the same concentrations and in the same volumes as with colloidal solutions. We used high-purity ICG from Sigma – Aldrich.
In the case of conjugation of ICG monomer with Ag2S QDs (2.2 nm), the increase in the dye luminescence intensity under excitation with a wavelength of 660 nm by 6 times is observed. It is a result of a decrease in its polymethine chain mobility due to the coordination interaction of sulfo groups (SO3-) with silver at the sites of Ag2S / TGA QD interface with a low ligand coating. QY of ICG associated with QDs increases by 5 times, and the luminescence lifetime increases by 1.5 times. The sensitization process has saturation. The increase in the dye fraction in associate does not lead to an increase in the sensitization efficiency. Observed regularities provide the increase in the intensity of IR luminescence excited in hybrid associates of colloidal Ag2S/TGA QDs and ICG dye.

The control of Ag2S / TGA QDs luminescence position with respect to the dye J-aggregates provided the conditions for changing the energy transfer between components in hybrid associate. The conjugation of Ag2S / TGA QDs (2.2 nm) with dye J-aggregates provides luminescence quenching excited by 660 nm in QDs band (900 nm) due to non-radiative resonance transfer of electron excitation energy from the recombination luminescence centers of nanocrystals to ICG J-aggregates. The association of ICG J-aggregates simultaneously with two different-sized Ag2S / TGA QDs (2.2 and 3.7 nm) having luminescence in the region of 900 nm and 1040 nm leads to luminescence quenching excited by 660 nm in the first band and its intensity increases in the second due to the exchange of electron excitations through the "intermediary" that is ICG J-aggregate. The sensitization efficiency is 0.33. This technique provides a transition from the first therapeutic window (NIR-I, 700-950 nm) to the second (NIR-II, 1000-1700 nm). It can allow high to increase the imaging in vivo resolution.

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References

Multi-walled carbon nanotubes and nanodiamonds degradation in human macrophages

E. K. Tarasova\textsuperscript{a}, A. G. Masyutin\textsuperscript{a}, M. V. Erokhina\textsuperscript{a}

\textsuperscript{a}Lomonosov Moscow State University, Moscow, Russian Federation

shalioto6@gmail.com

Multi-walled carbon nanotubes (MWCNT) and nanodiamonds (NDs) are the most popular carbon nanoparticles (1-100nm particles, which consist mostly of \(sp^2\)- and \(sp^3\)-carbon respectively). By 2018 global market of MWCNT was valued at around 4.55 billion USD and will increase to 9.84 billion USD in 2023, while European market of NDs will increase to 140 million USD by 2025. These nanoparticles are widely applied in polymer production, electronics and power engineering. In these fields, the industrially manufactured nanomaterials are used. Such nanomaterials demonstrate high heterogeneity of sizes and shapes, tend to aggregate in water suspensions and possess numerous defects in their structure. In addition, NDs and MWCNTs are a promising material for targeted drug delivery in cancer therapy, although more homogenous and less defective laboratory-synthesized nanomaterials are used in these approaches.

As the application of these nanomaterials is expanding constantly, their production volumes are increasing as well as the chance of their contact with living system. Unfortunately, the fate of internalized nanoparticles remains unclear. It was shown that nanoparticles may enter the organism through respiratory or digestive systems or via injections. After entering the organism, some nanoparticles are attacked by specialized phagocytes (macrophages and neutrophils) and may undergo processes of intracellular or extracellular oxidative degradation, which occurs with the participation of reactive oxygen species. Existing studies are based on laboratory-synthesized MWCNTs, while industrially manufactured nanotubes are much more common, and are more likely to be internalized by living organisms. Studies that investigate NDs
intracellular and extracellular degradation are extremely rare, thus the processes remain under-explored.

Thus, the main goal of this experiment was to study industrial MWCNTs and NDs degradation in human macrophages under the effect of extracellular and intracellular oxidizers.

In present study, we used detonation nanodiamonds (“Tekhnolog” Special Design Engineering Bureau (Federal State Unitary Enterprise), Saint Petersburg, Russian Federation) and multi-walled carbon nanotubes synthesized with chemical vapor disposition (NanoTechCenter Ltd, Tambov, Russian Federation). In order to study their degradation by human macrophages, THP-1 cells (5×10^5 cells/ml) were incubated with these nanoparticles for 10 days (macrophage differentiation was induced with 100 nM phorbol ester). For further investigations we analyzed: (1) non-internalized nanoparticles extracted from culture media (extracellular degradation model); (2) internalized nanoparticles – the cells were lysed by hypotonic shock and obtained cell lysate was examined (intracellular degradation model); (3) macrophage ultrastructure for internalized nanoparticles detection and localizing cellular compartment where the degradation occurs.

Multi-walled carbon nanotubes are elongated hollow cylindrical nanoparticles. The outer diameter varies from 20 to 90 nm, the inner diameter – 2-10 nm. MWCNTs’ length is highly heterogenic and may reach 2-3 μm. Nanodiamonds display more homogeneity in their shapes and sizes (4-5 nm) and their structure consists of so-called “diamond core” covered with graphite. Methods of conventional and analytical transmission electron microscopy were used to analyze the morphological and chemical alterations of nanoparticles. In addition, we used electron diffraction to prove the crystallinity of nanomaterials: NDs and MWCNTs both display specific electron diffraction patterns while amorphous structures do not.

After 10th day of incubating MWCNTs with human macrophages, the following results were obtained: (1) the extracellular MWCNTs’ outer diameter remained constant, while the inner diameter increased, which indicates the processes of degradation proceeding outward; (2) MWCNTs internalized by macrophages display significant wall deformation resulting in morphology alterations such as channel disappearing. This indicates destruction of the graphene layers from the outer surface as well as from the inner surface of the
nanotubes; (3) in macrophages, MWCNTs are detected inside the endosomes of different sizes; their crystallinity was confirmed using electron diffraction. Similarly, we observed numerous clusters with high electron density inside the endosomes; these clusters lack any diffraction pattern. We assume these clusters with high electron density are clusters of amorphous carbon, i.e. the remnants of completely degraded MWCNTs.

Both non-internalized and internalized nanodiamonds maintain their morphology after incubation with human macrophages. Inside the macrophages, NDs were detected as aggregates (30-500 nm) with high electron density inside the endosomes of different sizes, their crystallinity is confirmed using electron diffraction.

Using energy-dispersive X-ray spectroscopy (EDX) we demonstrated the decrease of oxygen levels in MWCNTs which underwent extra- or intracellular oxidation, while in case of NDs we observed increase of oxygen levels. This demonstrates different mechanisms of nanoparticle oxidation in macrophages.

The results obtained demonstrate different degradation rate of the experimental nanomaterials after extra- and intracellular oxidizing. Using this model, we observed that macrophages may completely reduce some MWCNTs to amorphous carbon in 10 days and oxidize the surface of diamond nanoparticles. Apparently, these processes take longer time; therefore, in case of longer exposure time more evident degradation may be expected. The propensity of nanoparticles for degradation via cellular oxidizers may be important for nanobiosecurity, when the potential harm must be estimated before their application.
Fractal properties of CdTe quantum dots dendrites

O. M. Kushchenko\textsuperscript{a}, L. N. Borodina\textsuperscript{a}, S. S. Rudyi\textsuperscript{a} and Y. V. Rozhdestvensky\textsuperscript{a}

\textsuperscript{a}ITMO University, Saint-Petersburg, Russia

kuschenko\_olga@mail.ru

Today the controlled self-assembly is extensively studied in nanostructure physics due to cheapness and ease of implementation in infrastructure. In that research quantum dots (QD) are of special interest because of their special properties (broad absorption bands, narrow luminescence spectrum, the quantum-confined effect, etc.). One way to QD colloidal solution self-assembly is dendritic structure formation (figure 1). The method of QD self-assembly on a dendritic ligand matrix vacancy is of interest through the harvesting, transfer, and concentration of light energy is possible.\textsuperscript{1} Such structures represent a potentially promising system for solar energy harvesting.\textsuperscript{2}

Note that only optical properties of QD ligand dendrites are currently being studied.\textsuperscript{3,4} However, dendrite has a branching shape that makes its structure properties, such as the fractal dimension of the ligand matrix, studying possible. In the present paper, we considered the characteristics of dendrites, which were grown by CdTe quantum dots colloidal solution with different concentrations. Dendrites spectrums were studied with a confocal microscope Zeiss LMS-710. After calculations of the fractal dimension by the box-counting method\textsuperscript{5}, the correlation between local luminescence spectral peak and local fractal dimension of the dendritic ligand matrix was discovered. The results open up new possibilities for dendrites characteristics studying and make evaluating the structural dependence of dendrites optical properties on the topological characteristics of the ligand matrix possible.
**Figure 1.** Fluorescent images of dendrite formed by water-solubilized CdTe quantum dots upon their incubation in the aqueous droplets at $5 \cdot 10^{-6}$ M concentration

**References**

Temperature and magnetic field quantum sensing using spin color centers in SiC

I. D. Breev, A. N. Anisimov, P. G. Baranov

Ioffe Institute, Saint-Petersburg, Russia

breev.ilia.d@mail.ioffe.ru

Atomic-scale spin color centers in silicon carbide (SiC) possess unique optical properties and long spin coherence times under ambient conditions, what makes them increasingly valuable objects alike for fundamental research and applications in the form of temperature and magnetic field sensors. Centers are characterised by spin-dependent optical cycle able to create optical spin alignment. It is possible to operate and detect their spin state using optically detected magnetic resonance (ODMR) method.

Silicon carbide is chemically stable and isn’t toxic. Also, it has many crystallographic polytypes with different characteristics. The spin center in view is negatively charged silicon vacancy exited by neutral carbon vacancy located along the crystalline axis c, so-called V-centers. In difference with widely known NV-centers in the diamond, they have photoluminescence in the near-infrared spectral region, which corresponds to transparency window in biology and fiber optics. It can be beneficial for the magnetic field and temperature measurements in depth of biological tissues with a confocal microscope or using optical fiber.

In our research, we focus on determining the possibilities of the magnetic field and temperature sensing using V-centers. They form deep levels in the bandgap, ground and excited spin state has S=3/2 and split into two double degenerated sublevels in zero magnetic fields. Spin manipulations are possible in view of the natural mechanism of optical-induced alignment of level populations of V-centers. Changes in these populations under resonance radio-frequency (RF) excitation in the ODMR or due to physical phenomena such as the level anticrossing or cross-relaxation strongly affect the photoluminescence (PL) intensity. Resonant changes of PL intensity can provide us information about the local field in the excitation region with spin color centers or local temperature.
Recent experimental results show the temperature-dependent cross-relaxation signal of V-centers in SiC. Fig.1 demonstrates a temperature shift of V-centers cross-relaxation line in 15R-SiC in the region of 35-40 °C. Also, we performed an ODMR experiment with temperature sweep, which is able to provide information only about temperature-dependent signals. Furthermore, recently we presented ODMR with “hole burning”, that can be applied for magnetic field measurements with better precision\(^2\). To increase the spatial resolution, we developed an approach to the detection of low magnetic fields and temperatures using an ensemble of V-centers in a SiC nanocrystal placed on the probe of a scanning atomic force microscope.

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**Figure 1.** Demonstration of cross-relaxation line temperature shift of V-centers in 15R-SiC.

**References**

Nanoporous silicate glass as an excellent matrix for preserving luminescent properties of carbon dots

E.A. Stepanidenko\textsuperscript{a}, I.A. Arefina\textsuperscript{a}, P.D. Khavlyuk\textsuperscript{a}, A. Dubavik\textsuperscript{a}, D.A. Kurdyukov\textsuperscript{b}, A.V. Fedorov\textsuperscript{a}, E.V. Ushakova\textsuperscript{a,c}, A.L. Rogach\textsuperscript{a,c}

\textsuperscript{a}ITMO University, Russia

\textsuperscript{b}Ioffe Physical-Technical Institute, Russia

\textsuperscript{c}City University of Hong Kong, Hong Kong

el.ushakova@gmail.com

Carbon dots (CDs) are a novel and promising class of luminescent nanomaterials showing many advantages, e.g. simple and low cost synthesis. Since CDs can be fabricated in the colloidal solutions, they can be embedded into different media, including polymers and solid-state matrices\textsuperscript{1}. Therefore, CDs are perspective in bioimaging, photocatalysis, sensors, and photonic devices. Here we investigate the optical properties of CDs incorporated into nanoporous silicate glass matrix (NSM), which can be used as active media in photonic devices.

The composite material was fabricated by embedding of CDs (average size 3-5 nm) into NSM (pore diameter of 8 nm) by the capillary method\textsuperscript{2}. A reference sample was obtained by drop-casting method of an aqueous solution of CDs on the glass substrate. Optical imaging shows that CDs were evenly distributed in the NSM (Fig. 1a). We observe a slight decrease in average photoluminescent (PL) lifetimes (\(\tau_{av}\)) of CD in NSM (8.3 ns) compared to \(\tau_{av}\) of CDs in solution (12.3 ns). At the same time, the PL peak is red-shifted by 50 nm compared CD’ solution (Fig. 1b). The time-resolved PL analysis also shows that the \(\tau_{av}\) increases with the PL wavelength with saturation at about 500 nm, which corresponds to the PL peak position (Fig 1c). This fact suggests that CDs do not form aggregates in the matrix pores in contrast to the weakly luminescent reference sample of drop-casted CDs on the glass substrate. In contrast, average PL lifetime of CDs on the glass slide is decreased by factor of 4.
Another interesting fact is that the average PL lifetimes are independent from the temperature of the sample (Fig.1c). This suggests that the electron-phonon interaction is weak both in CD@NSM and CDs on the glass.

In summary, we have shown that CD embedding into the nanoporous silicate glass matrix allows preserving the PL signal at the high level with the 50 nm PL band shift and slight decreasing of the PL lifetimes. Thus, the proposed fabrication method of composite materials based on CDs may be used as powerful tool for development of active optical media for future photonics.

References

DNA nanomachine suppressing the reproduction of Coxsackievirus B3

M.A. Misiurinaa, K.P. Chalenkoa, A.S. Volobuevb, V.V. Zarubaevb,
D. M. Kolpashchikovacd, E. I. Koshela,
aLaboratory of Solution Chemistry of Advanced Materials and Technologies,
ITMO University, St. Petersburg, 191002, Russian Federation
bDepartment of Virology, Pasteur Institute of Epidemiology and Microbiology,
St. Petersburg, 197101, Russian Federation.
cChemistry Department, University of Central Florida, Orlando, USA
dBurnett School of Biomedical Sciences, University of Central Florida, Orlando, USA

misyurina@scamt-itmo.ru

The Coxsackievirus B3 (CVB3), a member of the genus Enterovirus within the family Picornaviridae, is a primary causative agent of virus-induced myocarditis and dilated cardiomyopathy 1, 2. The chronic sequela of CVB3-induced myocarditis, dilated cardiomyopathy, is responsible for approximately 50 % of the cardiac transplants registered annually worldwide 3, 4. Unfortunately, there is no specific therapeutic agent available to address CVB3-induced myocarditis5, 6. Conversely, it may be possible to prevent the occurrence of CVB3-mediated myocarditis through vaccination, but no commercial vaccines currently are available for use in humans6.

RNA interference and Antisense Oligodeoxynucleotides-based technologies also have been developed to prevent the viral infection but selection an appropriate agent for antiviral therapy is still an urgent task.7, 8

In this study, we suggest to use the deoxyribozyme-based DNA nanomachine as an agent for gene therapy against Coxsackie viruses B3. Deoxyribozymes (Dz) are the DNA-enzymes having a catalytic activity which are able to cleave RNA9. The CVB3 viral genome consists of 7400 bases, and a single open reading frame flanked by 5’ and 3’ non-translated regions (UTRs) at the termini. The 5’ UTR contains an internal ribosome entry site (IRES) and mediates translation of positive-sense viral RNAs6. Viral IRES elements are organized in modules that are phylogenetically conserved10. Thereby this element of viral RNA was chosen as a target 8. For this study, genome analysis
of a large number of serotypes was carried out and a universal landing site for deoxyribozymes was found. Two synthetics short RNAs were synthesized for two deoxyribozyme. One of them has A/U cleavage site, another one G/U (Fig. 1). These pairs were tested under physiological conditions. Deoxyribozyme 2 (with G/U cleavage site) appeared much better in cleaving the target (8.7% in the case of Dz1 and 61.6% Dz2). Moreover, these two deoxyribozymes were tested with twice longer RNA (60 nucleotides) and Dz2 still was more effective than Dz1. As a result, Dz2 was chosen for future work.

**Figure 1.** The 2 secondary structures of RNA1 (a) and RNA2 (b).

As a positive control for experiment in cell culture, Phosphorothioate Antisense Oligodeoxynucleotide (AS-ODN) which is complementary to the site that is located at the proximate terminus of the 5’ UTR has been used. Transfection of Vero cells with AS-ODN was conducted with Lipofectamine 2000 or 3000. Our primary results showed the virus titer was decreased on 0.2 lg TCID50 using Lipofectamine 3000 as a transfection agent for AS-ODN while the transfected AS-ODN with Lipofectamine 2000 didn’t demonstrate antiviral activity. Moreover, we noticed the antiviral activity of Lipofectamine 2000 without AS-ODNs. It can be explained by damages in viral replicative complexes on the infected cell’s membrane.

For our further in vitro experiments, the DNA nanomachine was designed. This structure consists of the Dz2 and three antisense
oligodeoxynucleotides fixed to the platform (Fig. 2). Some of the phosphodiester bonds within components of the DNA nanomachine were replaced with phosphorothioates for protection against cell nucleases.

**Figure 2.** Complex of RNA with DNA nanomachine construction

This genetic construction will be tested on Vero cells and may be considered as a potential agent to create a versatile remedy for the most Coxsackie serotypes.

**References**

Fabrication of functional relief on polyvinyl chloride surface by nanosecond laser microtexturing

I. V. Krylach\textsuperscript{a}, S. I. Kudryashov\textsuperscript{a,b}, R. O. Olekhnovich\textsuperscript{a}, G. V. Odintsova\textsuperscript{a}, M. K. Moskvin\textsuperscript{a} and M. V. Uspenskaya\textsuperscript{a}
\textsuperscript{a} ITMO University, St. Petersburg, Russia
\textsuperscript{b} Lebedev Physical Institute, Moscow, Russia

irina-krylach93@mail.ru

The ability to synthesize polymers of a given chemical composition with controlled physical and chemical parameters allows them to be used to create microfluidic devices. The high optical transparency, mechanical strength and relative cheap cost of polyvinyl chloride provides an effective application as a coating to create a functional relief\textsuperscript{1}.

Surface textures were created on the MiniMarker2 workstation by raster scanning in a series of lines (10 lines / mm) in the form of columns with a period of 100 µm. Laser fluence was varied from 11 to 21 J/cm\textsuperscript{2} with a step of 2 J/cm\textsuperscript{2}, scanning speed was 500 mm/s, pulse duration 100 ns, wavelength 1064 nm.

In the present work, polyvinyl chloride (PVC) with a mass concentration of 8% was used as a coating.

The substrate was 50 µm thick copper foil.

The contact angle of the structures with water was determined using a DSA 100 KRÜSS tensiometer (Germany) by the method of a lying drop. The contact angle of the droplet with the polymer surface is 71°.

Figure 1 shows photographs of water at the surface structured with different values of laser power. It can be seen from the figure that the contact angle of the drop with the structured surface of the PVC changes by 50°.
The obtained various surface relief textures demonstrate a sharp drop (~50°) of the water contact angles to superhydrophilic ones, which allows the use of PVC for the manufacture of microfluidic devices with autonomous directional flow\textsuperscript{2,3}.

**Reference**


**Figure 1.** Water wetting angle of PVC structured surface at different energy density values:

- a) 11 J/cm\textsuperscript{2}
- b) 13 J/cm\textsuperscript{2}
- c) 15 J/cm\textsuperscript{2}
- d) 17 J/cm\textsuperscript{2}
- e) 19 J/cm\textsuperscript{2}
- f) 21 J/cm\textsuperscript{2}.
The effect of the Schottky barrier at the PbS / metal junction on the charge transport properties

D. A. Onishchuk, P. S. Parfenov

Center of Information Optical Technologies, ITMO University, Saint Petersburg 197101, Russia

onischuk.dmitry@gmail.com

In general, a Schottky barrier (SB) is a potential barrier in the metal–semiconductor junction. The SB takes place in nanocrystal (NC) optoelectronic devices, FET sensors with metal electrodes etc. The one blocks charge carriers and leads to nonlinear sensitivity and J–V characteristics of mentioned devises. The SB height depends on the difference between of metal work functions and semiconductor electron affinity, charge carrier density, type of conductivity and interface conditions. Additionally, the SB height could be higher due to the Fermi level pinning. When both electrodes form SB, which form the back-to-back diode circuit, the current of the device become determined by reverse current of SB.

Here we describe the influence of a SB on the J–V characteristic and mobility of charge carriers of EDT-treated (1,2-ethanedithiol) PbS NCs film, the size PbS NCs is 3.6 nm. In this work we use gold (5.1 eV, device 1) and silver (4.2 eV, device 2) cathodes, which were deposited directly on the top of NCs film, and we use ITO (4.7 eV) as an anode. J–V characteristics were measured by Ossila I-V Test System. Devices were stored on the ambient atmosphere.

On the first day both devices showed slightly asymmetric conductivity with a dominant current under forward bias and ohmic reverse current for device 1 (Fig. 1, a), which indicate of the formation of a SB and partly ohmic contact in case of the gold electrode. Note, device 1 demonstrated higher barrier (Table 1). On the next day SB heights became lower for both devices and the partial ohmic conductivity remained, but the device 2 became closed at small reverse bias (Fig. 1, b). Device 2 was probably affected by metal oxidation, and under reverse bias the tunneling current was observed.
**Figure 1.** J–V characteristics of EDT PbS the device 1 with gold (left scale) and the device 2 with silver (right scale) cathode (a) on the first day and (b) on the second day.

The SB value was calculated by eq.14:

\[ J_0 = A'T^2e^{\frac{-q\psi_B}{kT}}, \]

where \( J_0 \) is saturation current, \( A' \) is Richardson constant (98 Acm\(^{-2}\)V\(^{-2}\)), \( T \) is a temperature, \( q \) is elementary charge, \( \psi_B \) is SB value, \( k \) is Boltzmann constant.

<table>
<thead>
<tr>
<th>Type of cathode</th>
<th>The SB height, eV</th>
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<tr>
<td></td>
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<tr>
<td>gold</td>
<td>0.33</td>
</tr>
<tr>
<td>silver</td>
<td>0.29</td>
</tr>
</tbody>
</table>

In conclusion, a SB leads to formation nonlinear J–V curves, but the SB height depends on the cathode material and decreases with time. The gold electrode provides higher barrier and less current in both directions, but more linear JV due to partly ohmic contact. The silver electrode forms lower barrier that provides more current and forms oxide interlayer. Furthermore, using metals with oxidation can provide the forward current decrease and provide tunneling.

**References**

1. Choi H.H. et al., Critical assessment of charge mobility extraction in FETs, Nat. materials 17, 2–7 (2017).
Enhancement of photoluminescence of carbon dots in hybrid structures based on granulated silver films

E. G. Shmagina, E. A. Konshina, D. P. Scherbinin, P. D. Khavlyuk, M. S. Stepanova

ITMO University, Saint-Petersburg, Russia

lizakoritsa@gmail.com

The optical density spectra of granulated silver films of different thicknesses were studied and the photoluminescence (PL) spectra of hydrophilic carbon dots deposited on their surface from a solution. The twofold plasmon enhancement of the PL intensity was obtained, which allows the use of these hybrid structures in biosensor chips.

Carbon dots (C-dots) have several advantages over semiconductor quantum dots, including their simple synthesis, low toxicity, and high biocompatibility. Photoluminescence of C-dots is a key property for their application. It can be enhanced as a result of their exciton-plasmon interaction with metal nanostructures.

In this work, we studied granular silver films on a glass substrate with a thickness of 2, 4, and 10 nm, obtained by resistive evaporation in vacuum. Hydrophilic C-dots were obtained by condensation polymerization from citric acid and ethylenediamine with further carbonization. C-dots were deposited on a solid surface by centrifuging their solution. We studied the PL of C-dots near the surface of silver nanoparticles at an excitation wavelength of 405 nm using a confocal microscope. To reduce nonradiative energy transfer in hybrid structures, five layers of a one percent solution of polystyrene in toluene were applied to the silver surface.

A twofold plasmon amplification of the PL was obtained in hybrid structures with 10 nm Ag films (Fig. 1). Figure 2 shows the overlap of optical density spectra of silver films of different thickness after annealing at 200°C with the PL spectra of the C-dots nanostructure. It can be seen that with an increase in the thickness of the silver film, an increase in plasmon resonance
is observed. The enhancement of PL is facilitated by an increase in the absorption cross section and the Purcell effect.

The possibility of plasmon amplification of PL C-dots in thin-film hybrid structures was shown for the first time. This opens up new possibilities for their use in photonic and other devices.

**Figure. 1** Luminescence spectra of multilayer Ag/polystyrene/C-dots structures with a gravimetric thickness of granulated silver films 2, 4 and 10 nm thick (samples 1, 2 and 3, respectively) and the control structure of polystyrene/C-dots (4)

**Figure. 2** Overlap of the optical density spectra of granulated silver films with a thickness of: 2 nm (1); 4 nm (2); 10 nm (3) and photoluminescence of the C-dots nanostructure obtained in 12 deposition cycles (4)

**References**

Impact of external magnetic field on the spatial arrangement of luminescent SPION/CdSe/ZnS nanocomposites in microfluidic device

U.A. Timkina\textsuperscript{a}, I.A. Reznik\textsuperscript{a}, A.A. Matyshkina\textsuperscript{a}, A.U. Dubavik\textsuperscript{a} and A.O. Orlova\textsuperscript{a}

\textsuperscript{a}ITMO University, Saint Petersburg, Russia

Timkina.yu.a@gmail.com

Magnetic nanoparticles are a new kind of nanostructured materials that are actively investigated for different application such as biochemistry, molecular biology, medicine\textsuperscript{1}. Distinctive features of magnetic nanoparticles are their sensitivity to an external magnetic field, as well as their superparamagnetic properties, allowing the use of magnetic nanoparticles, for example, super paramagnetic iron oxide nanoparticles (SPIONs), as an effective contrast agent for MRI.\textsuperscript{2} Due to the high degree of functionalization of the magnetic nanoparticles surface, it is possible to form systems with various functional shells in order to achieve the goals pursued. For example, nanocomposites (NCs) that are formed by coating SPION core with CdSe/ZnS shells show the luminescent properties, like quantum dots, and the ability to respond to a magnetic field.\textsuperscript{3} In addition to the creation of NCs, there is an urgent question of developing methods for the implementation of magnetically controlled delivery of the nanocomposites.

The aim of this work is to study the stability of the hydrophobic microdroplet of SPION/CdSe/ZnS NCs in the fluid flow under the external magnetic field. We have used 0.5 µl microdroplets of SPION/CdSe/ZnS NCs hexane solution injected into glass capillary with the diameter of 0.15 cm filled by water. The magnetic field applied to the samples was 2230 G. Nanocomposite microdroplets introduced in distilled water in capillary tube were studied under static and dynamic conditions of liquid flow. The fluid flow rate was varied from 0.057 to 566 cm·min\textsuperscript{−1}. The study was carried out
using a luminescent confocal microscope LSM710 in transmission and luminescence modes.

It was found that a position and shape of NC microdroplet introduced into glass capillary depend on liquid flow rate. The first signs of deformation of the NC microdroplet appeared at the flow rate equal to 370 cm·min⁻¹, but the deformation of the droplet did not happen even at the speed of 565 cm·min⁻¹. It demonstrates that the SPION/CdSe/ZnS NCs can be run by external magnetic field efficiently in vessels up to 0.15 cm in diameter, because blood flow there is 540 cm·min⁻¹.¹

**References**

Transparent ferromagnetic composite for applied magnetooptics

Zh. G. Snezhnaia\textsuperscript{a}, L. A. Sokura\textsuperscript{a}, D. Yu. Panov\textsuperscript{a}, V. A. Spiridonov\textsuperscript{a}, A.V. Apanasevich\textsuperscript{a}, and Ya. N. Kovach\textsuperscript{a}

\textsuperscript{a}ITMO University, Saint-Petersburg, Russia

genevievev-v@yandex.ru

The development of an increasing magneto-optical sensors sensitivity material based on the Faraday principle is a problem of current interest.\textsuperscript{1}

A polarization plane angle transmitted through the substance radiation rotation scheme registration is implemented in such sensors, which implies the use of an optically transparent material as the sensor’s active element. Simultaneously, it is rational to choose a material with a high Verdet constant to increase the device sensitivity, however generally such materials are not optically transparent. A ferromagnet nanoparticles a with a large Verdet constant embedded in a transparent matrix optically transparent composite creation is an interesting solution to this problem. Recently, such granular structures have received the great attention.\textsuperscript{2}

In an addition to the issue of strong absorption of radiation in a bulk ferromagnetic material, there is a problem of controlling the material temperature gradient, since the Verdet constant is a temperature-dependent quantity. Thin-film structures avoid this problem.

Thus, there is a problem to develop the material and to study its properties, to select compatible materials used as a matrix and the embedded in it components. Sol-gel technology is suitable for this.

This paper presents the development data of a EuS ferromagnet nanoparticles embedded in a PMMA polymer matrix composite structure received by the sol-gel technology. The composite structure was simulated in the Comsol Multiphysics mathematical package to obtain an effective magneto-optical material. The required EuS nanocrystal sizes and the distances between them were determined. The material development experimental data, resulting structures x-ray data analysis are presented. A
current sensor element active implementation scheme based on the developed thin-film material is suggested.

References

Diffraction phase microscopy for cell visualization

A. O. Georgieva\textsuperscript{a}, N. V. Petrov\textsuperscript{a}

\textsuperscript{a}ITMO University, St. Petersburg, Russia

georgieva@itmo.ru

The method of digital holographic microscopy allows non-invasive quantitative analysis of cell cultures due to registration of phase delay introduced by a transparent object. Quantitative phase imaging (QPI), which measures the optical map of the path length of a sample, has become a rapidly developing field with many biomedical applications\textsuperscript{1}.

QPI methods used to visualize cells make it possible to quantify the biophysical parameters of cells, such as dry mass and intracellular refractive index based on optical phase shifts measurement. Based on these parameters it is possible to extract information about cell volume, protein concentration, cell permeability, cell apoptosis or necrosis. Several particular trends in the development of cell research using QPI can be distinguished: the study of fluctuations of the cell membrane, recognition and classification of cells, profiling of individual cells and correlation diagnostic methods, three-dimensional visualization of cells in the flow channel, the study of the internal structure of red blood cells\textsuperscript{2}.

The main obstacles to obtaining quantitative phase images with high sensitivity is phase noise due to mechanical vibrations, air vibrations, and speckle noise due to high-coherent radiation. These factors usually affect any interferometric system. In addition, for the study of cell cultures in vitro, it is convenient to use optical schemes with a vertical direction of the optical axis. The combination of these factors leads to the use of diffraction phase microscopy (DPM)\textsuperscript{3} with a low-coherent radiation source, which is also a common path interferometer, which reduces noise from external vibrations.

In this work we present low-cost diffraction phase microscope in a vibration-resistant optical cage system with optomechanical components manufactured using 3D printing technology. Two configurations have been used: high-coherent laser and low-coherent LED as light source.

Images of fixed HeLa cells obtained by high-coherent and low-coherent DPM configurations are presented in Fig. 1. Image obtained by low-coherent
DPM are more detailed, because for laser DPM, coherent artifact noise due to appearance of parasitic fringes reduces the image quality.

**Figure 1.** Image of HeLa cell obtained by high-coherent (a,b) and low-coherent (c) radiation. a) Phase image; b-c) amplitude image

To date, we did not succeed in obtaining phase images of the cell in a low-coherent mode, but further modifications of the setup will help us to achieve this goal. DPM modifications will also optimize the conditions for non-invasive monitoring of various cell culture lines *in vitro*, studying their dynamics under the influence of external factors, or studying internal cell processes based on data extracted by holographic methods. For example, it is easy to introduce external radiation in optical scheme for investigation of light-induced effects. In particular, there is an option of femtosecond laser radiation input through a dichroic mirror for cell membrane optoporation and real-time study of cellular reaction.

**References**

Chiral nonluminescent aggregates of chlorin e6 on quantum dot surfaces

A. K. Visheratina\textsuperscript{a}, F. Purcell-Milton\textsuperscript{b}, Y. Gun’ko\textsuperscript{a, b}, and A.O. Orlova\textsuperscript{a}

\textsuperscript{a}\textit{ITMO University, Saint Petersburg, Russia}
\textsuperscript{b}\textit{School of Chemistry and CRANN, University of Dublin, Trinity College, Dublin, Ireland}

a.k.visheratina@gmail.com

Despite the widespread use of tetrapyrroles\textsuperscript{1} and, in particular, chlorin e6 (Ce6), in photodynamic therapy (PDT) of cancer, they have many side effects\textsuperscript{2}, and one of the approaches to creating a new generation drug is the formation of hybrid nanostructures (HNs) based on semiconductor quantum dots (QDs) with tetrapyrrole molecules\textsuperscript{3}. The functionality of these HNs can be estimated via the efficiency of energy transfer from QDs to tetrapyrroles, as well as photoluminescence quantum yield (PL QY) of tetrapyrroles.

Despite the active interest and a large number of studies devoted to the QD/Ce6 HNs as a new drug for PDT\textsuperscript{4}, the reason for the decrease of the PL QY of Ce6 with an increase of its concentration in QD-based HNs has not been established.

Previously, by absorption spectroscopy methods, it was found that phthalocyanine molecules form nonluminescent aggregates in QD-based HNs, which leads to the decrease of energy transfer efficiency and PL QY of phthalocyanine\textsuperscript{5}. It could be assumed that Ce6 also forms nonluminescent aggregates, however, in the absorption spectra there were no such apparent manifestations of Ce6 aggregation as in the case of phthalocyanine molecules, and only the monomeric form of Ce6 was observed in the PL spectra. Ce6 is a chiral molecule, and it was shown in Ref.\textsuperscript{6} that circular dichroism (CD) spectroscopy is a more sensitive method for studying the degree of aggregation of Ce6 compared to stationary absorption spectroscopy. It is important to note that this method has not been used previously to study photophysical properties of HNs based on QDs and tetrapyrrrole molecules. Therefore, we carried out the first comprehensive study of HNs using stationary absorption and PL spectroscopy, time-resolved PL microscopy, and also CD spectroscopy.
In this work, as a result of electrostatic interaction between Ce6 molecules and biocompatible ZnS:Mn QDs, QD/Ce6 HNs were formed. It was found by spectral-luminescent methods that with an increase of Ce6 concentration in a mixture with QD, PL QY of Ce6 significantly decreased. The shape and position of the PL bands of Ce6 corresponded to its monomeric form. However, an analysis of the CD spectra showed that the spectrum of Ce6 in HNs has a more complex shape different from that of Ce6 monomers. Analysis of the experimental data revealed that in addition to QD-bounded Ce6 monomers, there is a nonluminescent form of Ce6, which leads to a decrease of PL QY of Ce6.

Thus, the study of HNs based on QD and Ce6 using CD spectroscopy made it possible to establish the reason for the decrease in the PL QY of Ce6 in QD-based HNs. In turn, this allows to optimize the conditions for the formation of HNs and take a step forward in creating new-generation drugs.

References
Laser heating of luminescent semiconductor nanoplatelets as a novel way of micro-volume temperature control

D. Gozhalskii, M. Baranov, I. Reznik, S. Cherevkov, A. Dubavik, A. Veniaminov

ITMO University, Saint-Petersburg, Russia

gozhal.daniil@gmail.com

The problem of temperature measurements in micro-sized volume remains unexplored to date. One must admit that temperature doubtless affects various characteristics and properties of matter to any extent in most cases. Especially it concerns biological objects, which are widely being investigated by multiple means, e.g. laser scanning microscopes. The tightly focused laser beam can either accidentally destroy the valuable sample or intentionally burn out cancer cells, depending on the situation. Conventional thermometers used in daily life and in wide range of research are incapable of thermal measurements in microscopic volume by reason of low temperature resolution. Nevertheless, such issue may be solved by nanocrystals, responding to negligible thermal changes with own luminescence spectra. Hence, this work is dedicated to microscope’s laser heating, namely its effect on optical characteristics of semiconductor nanoparticles.

Figure 1. Nanoplatelets’ luminescence maximum wavelength dependence on temperature

The increasing temperature leads to reversible shift into long-wavelength region of luminescence spectral position. It can be seen in the
Fig. 1 that after several heating-cooling cycles there is still complete coincidence between wavelength among all measurements within a small error. It was previously shown that such parameters as luminescence intensity and spectral width have limited applicability for thermal experiments because of either low sensitivity, complicated temperature dependence, or being a relative quantity, but the decay time potentially may become a powerful criterion for temperature control after resolving its tricky mechanism.

Fig. 2 demonstrates how a focused laser beam heats up the nanoplatelets layer deposited onto a glass substrate by Langmuir-Blodgett technique (that is proved by shift in spectral position and corresponding temperature change). Using thermal calibration of specific nanoplatelets’ temperature sensitivity, we managed to estimate the sample’s temperature at the maximum laser power — it was about 130 °C. Reduction of scanning area also influences nanoplatelets’ temperature: it increases as expected.

Therefore, the approach described may be extremely perspective for measuring temperature in small volume, e.g. for living cells, as capable of operating with micro-areas.

**Figure 2.** Dependence of the luminescence wavelength maximum on laser radiation power (for nanoplatelets)

**References**

Confocal and time-resolved microscopy of alloyed quantum dots

M. S. Stepanova\textsuperscript{a}, V. Zakharov\textsuperscript{a}, A. Dubovik\textsuperscript{a} and A. Veniaminov\textsuperscript{a}

\textsuperscript{a}ITMO University, Saint-Petersburg, Russia

mary.s.stepanova@gmail.com

Results on luminescence of single semiconductor quantum dots (QDs) observed using a confocal scanning microscope LSM 710 (Zeiss) are presented. Visualization of single quantum dots (QD) requires a sufficiently low concentration. For this purpose, the initial solution of alloyed QDs, which were synthesized by the method\textsuperscript{1}, was diluted to reach as low surface concentration in on the top of the substrate as 10 µm\textsuperscript{-2}.

The luminescent image of the 5 × 5 µm portion of this sample is shown in Fig. 1, left. This image was obtained by a multichannel detector, which accumulated the fluorescence signal. Fig. 1 right shows the luminescence spectra from the area of 5 × 5 µm and from individual regions. The analysis of the luminescence spectra from the individual sites has shown that they have a smaller half-width relative to the ensemble and differ in the spectral position of the maximum intensity. These results suggest that we see single nanoparticles. The average spectrum obtained from the ensemble of quantum dots is the envelope for single nanocrystals.

\textbf{Figure 1.} Luminescent image of a 5x5 µm area (left) and spectra of PL intensity (right) from ensemble and of the single QDs (line color correspond to the regions in the image, left)

The obtained sample was also studied with time-resolved confocal fluorescence microscope MicroTime 200 (PicoQuant), which made it possible
to receive a time-resolved PL image and construct emission decays of the individual regions (Fig. 2). The data acquired are shown in Table 1 and indicate that the ensemble has shorter lifetimes than individual regions.

The fluorescence signal registered from single QDs is confirmed by the change in fluorescence intensity from these areas, which is the result of measurements with temporal resolution. Black bars on the background of emission show the transition of a single QD from a light state to a dark one during the time of laser scanning. This behavior can be interpreted as the blinking of single QDs, at which the particle switches from dark to light state.

![Time-resolved PL images](image)

**Figure 2.** Time-resolved PL images (left) and emission decays (right) of the ensemble and of the single QDs (regions shows left)

<table>
<thead>
<tr>
<th>Area</th>
<th>$A_1$ (Cnts)</th>
<th>$\tau_1$ (ns)</th>
<th>$A_2$ (Cnts)</th>
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</table>

**Table 1.** Fluorescence lifetimes of the QDs.

References

Luminescence of a Photoinitiator for Structured Polymerization

L. N. Borodina², M. S. Stepanova, V. V. Zakharov, A.V. Veniaminov
²ITMO University, St.Petersburg, Russia

lborodina98@mail.ru

Photopolymerization of a composite with luminescent nanoparticles (NP) in a structured light, e.g. interference field of two or more light beams, is a promising way to construct efficient 3D diffraction/emission elements, such as DFB-lasers. In such systems, photoluminescence (PL) of photopolymerization initiators may interfere with that of NPs or serve for diagnostic purposes. In the present study, PL of phenanthrenequinone (PQ) used as a visible-light initiator in several holographic materials¹, is examined in two model environments, methyl methacrylate (MMA) and CCl₄, of which only the former one is capable of polymerization (Fig.1.)

**Figure 1.** Microscopic images of a PQ solution in MMA with two square 100×100 µm areas previously exposed to 405 nm laser light, obtained with Zeiss LSM710 laser microscope in PL (left) and transmitted light DIC (right) modes, revealing PQ transformation and photopolymerization, respectively.

Both solutions of PQ in MMA and CCl₄ appear photosensitive, although in different manner, as parallel changes in UV-vis (Fig.2) and PL excitation (PLE) spectra (Fig.3) manifest. In the course of illumination, PQ phosphorescence² at 585 and 645 nm is replaced by rising blue PL that is attributed to substance(s) resulting from PQ phototransformation³. These apparent changes in PL would hardly harm 3D recording in non-luminescent composite materials; moreover, they can be applied for monitoring the photoreaction or patterning the interference structure being recorded; on the other hand, the PL of photoinitiators should be taken into account in the case
of luminescent nanoparticles included in the recorded material to create e.g. DFB structures. For such purposes, Irgacure 784 initiator that did not reveal any significant PL in the tests like those described in this contribution can appear a good alternative.

Figure 2. UV-vis spectra of PQ solutions in CCl₄ and MMA before (dashed lines) and after (solid lines) exposure to 470 nm illumination

Figure 3. UV-vis (dash-dotted), PL (solid) and PLE (dashed) spectra of PQ in MMA (left) and CCl₄ (right) solutions after exposure to 470 nm LED light

References

Nanofibers as promising materials for the third generation of solar cells

M. Bkkar*, R. O. Olekhnovich*, and M. V. Uspenskaya*

*ITMO University, Saint Petersburg, Russia

muhammad.bkkar89@gmail.com

Currently, as the demand for energy is growing rapidly in recent years, so it’s natural to worry about humanity’s long-term future, and become energy conversion and energy storage hot research topics. The solar cells present a promising solution to our clean and renewable energy needs. Recently, nanofibers have attracted much attention in solar cells due to their unique properties, so recent advances in the third-generation solar cells (polymer-based solar cells, dye-sensitized solar cells (DSSCs), and perovskite solar cells) are typically based on such as nanomaterials.

In this paper, we will present a review about recent achievements in nanofibers-based solar systems, which typically depend on structured nanofibers (hollow, mesoporous, core-shell and surface modified NFs), and we will discuss the advantages of the nanofibers for efficient charge separation, collection, and transport. Finally, challenges and ways of development of this technology will be observed.

References
Up-conversion enhancement and size changes of β-NaYGdF$_4$:Yb, Er, Tm nanoparticle by variation of synthesis parameters

A.A. Vidyakina$^a$, A.S. Mereshchenko$^a$

$^a$Department of Laser chemistry, Saint-Petersburg State University, Saint-Petersburg, Russia

vidyakina.aleksandra@mail.ru

Fluorescent nanoparticles β-Na$_x$Y$_x$Gd$_y$F$_4$:Yb$^{3+}$,Tm$^{3+}$ due to their optical properties have a great potential for applications in bio-imaging as fluorescent labels and imaging probes. We have studied the influence of the hydrothermal synthesis parameters on the luminescent properties of NaY$_x$Gd$_y$F$_4$ nanoparticles co-doped with Yb$^{3+}$, Tm$^{3+}$ and Er$^{3+}$. The factors affecting the size and shape of the upconversion nanoparticles also were deliberated in our work. The upconversion emission intensity of NaYGdF$_4$:Yb$^{3+}$, Er$^{3+}$/Tm$^{3+}$ can be improved by optimizing Gd$^{3+}$ content. It was found that higher Gd$^{3+}$ concentration leads to the decrease of the luminescence intensity.

The nanoparticles were synthesized by hydrothermal method. The morphology of the obtained nanoparticles was studied by transmission electron microscopy. They have hexagonal structures and size of around 800 nm. The up-conversion fluorescence of β-Na$_x$Y$_x$Gd$_y$F$_4$:Yb$^{3+}$, Tm$^{3+}$ nanoparticles dispersed in water was measured at 980 nm excitation wavelength. The sample exhibited blue luminescence, which originated from the $^1$D$_2 \rightarrow ^3$H$_6$, $^1$I$_6 \rightarrow ^3$F$_4$ transitions of Tm$^{3+}$.

The measurements where performed in the “Centre for Optical and Laser materials research”, “Interdisciplinary Center for Nanotechnology”, “Centre for Molecular and Cell Technologies” and “Cryogenic department” of research park of Saint-Petersburg State University.
References


Magnetite nanoparticles antimicrobial effectiveness against planktonic forms of bacteria and biofilms

V. I. Rumyantceva, V. I. Rumyantceva, E.I. Koshel, and V.V. Vinogradov

ITMO University, Saint-Petersburg, Russia

viktoriya_rumyantceva@scamt-itmo.ru

Compared to other transition metal oxide nanoparticles, magnetite (Fe₃O₄) does not have a strong antibacterial effect. At the same time, it also has almost no cytotoxic effect which leads to its biocompatibility and approval by the Food and Drug Administration (FDA) for medical use.

The following mechanisms are considered as mechanisms of antibacterial action: 1) electrostatic interaction with the cell wall, 2) the release of metal cations, and 3) the formation of active oxidative forms (Fig. 1).

![Figure 1. Mechanism of magnetite nanoparticles action on bacterial cell](image)

The sensitivity of different types of bacteria to a particular mechanism of exposure is due to the type and strain of bacteria. Thus, the most sensitive species in the case of a predominant oxidative effect on cells is Staphylococcus aureus. At the same time, in the case of the influence of electrostatic
attraction, where the charge degree (polarity value) of the bacterial membrane is of great importance, there is information about the specific antimicrobial effect of magnetite on gram-negative types of bacteria.

However, magnetite has a weak biocidal effect for individual use as an antibacterial agent. It has properties that allow it to stimulate or inhibit the antimicrobial effect of various antibiotic substances. In addition, pure magnetite is unstable and, once in a biological environment, immediately begins to electrostatically interact with other biomolecules, pro- and eukaryotic cells.

In this regard, magnetite nanoparticles particularly are more appropriate to use as the means of biocidal molecules delivery including transfer under the influence of a magnetic field. In recent years, a large number of biocide-conjugated magnetite nanoparticles has been developed which are in various degrees against not only planktonic forms of bacteria but also biofilms.

Thus, a ceramic composite material with magnetically controlled properties and high antimicrobial activity has been developed. The high efficiency of the composite is due to the synergistic effect of all its constituent components and the functionality of the composite as a whole.

The present studies are aimed at optimizing the method of obtaining an effective magnetically controlled composite and a comprehensive study of its effect on bacterial biofilms.

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