

Polymer based UV Induced Nanocomposites with Metal and Semiconductor Nanoparticles

A. A. Smirnov, A. Afanasiev, N. Bityurin

Abstract— The purpose of this review is to draw the readers' attention to the problem of in situ formation of nanoparticles of different kinds just within the polymer matrix by means of light irradiation. This offers an opportunity for patterning the initially homogeneous materials because the formation of nanoparticles strongly changes their optical properties. It would be very useful in photonics applications.

Index Terms— Metal nanoparticles, nanocomposites, semiconductor nanoparticles, UV irradiation.

I. INTRODUCTION

Photoinduced nanocomposites are materials consisting of a transparent, typically polymer matrix with introduced precursor molecules. Under irradiation, precursors undergo chemical transformations resulting in the formation of nanoparticles (NPs) (Au, Ag, CdS, CdSe, etc).

The most investigated are the so-called plasmon photoinduced nanocomposites with metallic NPs. The extinction spectrum of such NPs exhibits a very pronounced peak associated with plasmon resonance, when the optical frequency matches the frequency of collective oscillations of electrons with respect to positive ions constituting the metallic lattice. The optical properties of such NPs in dielectric matrix are well known and have been thoroughly described in [1]. For spherical NPs, the resonance frequency does not depend on their radii. However, if the size of NP exceeds the depth of the skin layer, the maximum of extinction shifts towards the longer wavelengths. The extinction spectrum strongly depends on the shape of the NPs, the spectrum of nanorods strongly differs from the spectrum of spherical NPs. The position of plasmon resonance slightly depends on the refractive index of the dielectric matrix, for spherical NPs an increase in the refractive index results in an increase in the resonance wavelength. Gold NPs in a typical polymer matrix with refractive index near 1.5 (e.g., PMMA) demonstrate a plasmon resonance near 530 nm, with silver NPs the resonance wavelength is about 420nm.

Photoinduced nanocomposites with semiconductor NPs

Anton A. Smirnov, Institute of Applied Physics Russian Academy of Sciences, Nizhny Novgorod, Russia, +78314164889, (e-mail: anton-smirnov@ufp.appl.sci-nnov.ru).

Andrey Afanasiev, Institute of Applied Physics Russian Academy of Sciences, Nizhny Novgorod, Russia, +78314164889, (e-mail: ava@ufp.appl.sci-nnov.ru).

Nikita Bityurin, Institute of Applied Physics Russian Academy of Sciences, Nizhny Novgorod, Russia, +78314164889, (e-mail: bit@ufp.appl.sci-nnov.ru).

This work was funded by the Russian Federal Agency for Scientific Organizations as a part of the State Assignment for the Institute of Applied Physics RAS under Project No. 0035-2014-0019.

are also intensely studied because of their unique luminescent properties. These properties are related to the existence of the room-temperature stable exciton levels in these nanoobjects. Thus, we use the term exciton nanocomposites for the materials containing semiconductor NPs. Techniques for the preparation of CdS and CdSe NPs (or quantum dots) are well developed [2]. However, in-situ formation of such objects directly in the polymer matrices by means of light irradiation is still a challenging problem.

In this mini-review, we sequentially consider the photoinduced formation of metal and semiconductor nanoparticles in a polymer matrix separately and the first attempts to obtain the different kinds of nanoparticles within the same sample.

II. COMPOSITES WITH METAL NANOPARTICLES

The most popular gold precursor is HAuCl_4 . This compound is good soluble in organic solvents, such as chloroform, toluene, etc, and in typical polymer matrices. Therefore, it is useful in film preparation for photoinduced nanocomposites by casting technique. A typical scenario of the gold NP formation in a polymer film looks as follows [3]. Initial PMMA film with HAuCl_4 has a maximum of absorption shown in Fig. 1a. The absorption peak at 320 nm corresponds to absorption by precursor. After UV irradiation, this absorption band vanishes, demonstrating the precursor depletion. After annealing of the irradiated film at 60-80 °C, the absorption band corresponding to plasmonic resonance of gold NPs starts growing, as it is shown in Fig. 1b. It is interesting that the shape of the extinction band almost does not change during the growth. It can be interpreted by that the size distribution of NPs is approximately constant and an increase in magnitude of the absorption peak is resulted from an increase in number density of the NPs.

It should be understood that if we speak about the polymer matrix for photoinduced nanocomposites, the samples obtained by polymerization are much more advantageous compared to the ones obtained by casting. The polymerization obtained matrices are real organic glasses that can be mechanically treated, achieving the optical quality of their surfaces. They are the real bulk materials. However, the obtaining of the photoinduced nanocomposite samples by polymerization faces difficulties. For instance, bulk radical polymerization of MMA containing HAuCl_4 appears to be practically ineffective because the precursor molecules react with monomer and with radicals driving the polymerization process. As a result, the gold atoms are extracted from the precursor molecules at the stage of

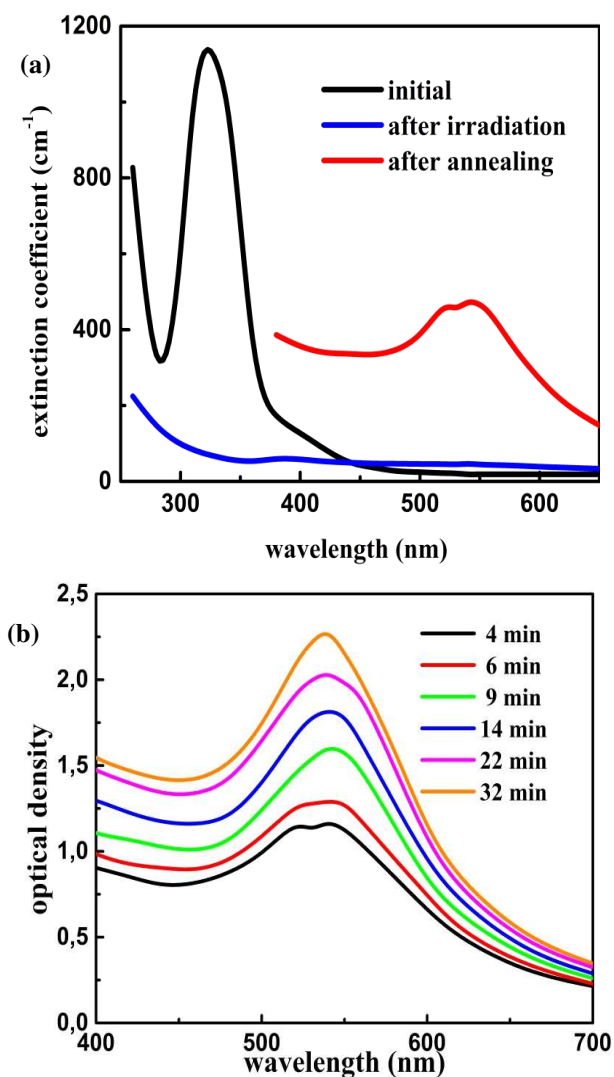


Fig. 1. Effects of the UV irradiation and the following heat treatment on the extinction spectrum of composite HAuCl₄/PMMA: (a). After UV irradiation the absorption peak at 320 nm corresponding to HAuCl₄ absorption vanishes, the subsequent heat treatment results in growing of the peak near plasmon resonance of Au nanoparticles (b). The growing of the extinction plasmon resonance peak due to heat treatment at 75 °C. (for details see [2]).

polymerization, leading to gold NPs precipitation during the sample preparation. In order to avoid this circumstance, the authors of [4] Agareva et al, used another precursor, namely tetrachlorogold (III) N-cetylpyridinium (Au-P16) , and employed special initiator and polymerization conditions published in [4], which allowed them to obtain a gold precursor containing PMMA matrix, avoiding the gold precipitation. Fig. 2 shows the corresponding samples after irradiation. Irradiation was performed by a XeCl excimer laser through a special mask. It is seen that the irradiated fields are red because they absorb green light corresponding to the plasmon resonance band, whereas the initial samples as well as the non-irradiated parts of the treated sample are optically transparent.

The mechanism of NPs formation is still under discussion. The simplest model suggests that under effect of irradiation the metal atoms are extracted from the precursor molecules. Because of the big difference in bond energies of noble



Fig. 2. HAuCl₄/PMMA sample obtained by bulk polymerization. Color parts are obtained by UV 20 min irradiation by XeCl laser through the mask and subsequent annealing over 3min at 160 °C. These colored domains contain Au nanoparticles (for details see [3]).

atom – noble atom and noble atom-polymer matrix, the solution of noble atoms in polymer matrix appears to be supersaturated and NPs are formed as a nuclei of a new phase in precipitation phase transition [5]. The same mechanism is valid for NPs formation in liquid but, contrary to the liquid, the mobility of nanoclusters in the solid matrix is hindered so that there is no need in stabilizers preventing cluster aggregation.

The opportunity to create some amount of the noble metal atoms just within the polymer matrix, where these atoms keep their ability to diffuse aggregating with each other to form NPs, is very interesting from both the practical and theoretical points of view. In particular, it makes actual the consideration of the nucleation and growth of NPs in inhomogeneous media, which is a further development of the theory of phase transition of the first order. The inhomogeneity can be connected either with the spatially inhomogeneous precursor destruction caused by irradiation or with the inhomogeneity of the matrix. The former can be provided by a focused laser beam in the direct writing approach to laser patterning, by laser beam interference, by the projection technique or by irradiation through the mask. The latter can be actual in the initially inhomogeneous media, or in the media where the inhomogeneity of the matrix is induced by the laser irradiation due to, e.g., laser swelling or laser densification phenomena changing the local density of the material. It is shown in [6] that it offers an opportunity to control over the spatial distribution of NPs. From this point of view [6] considers the effects of spatial modulations of both the diffusion coefficient of the aggregating atoms and the energetic part of the chemical potential of these atoms within the matrix. Both of these kinds of spatial inhomogeneity can be caused by the laser irradiation.

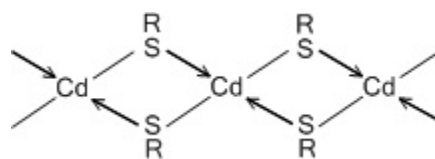


Fig. 3. Schematic view of coordination polymer of Cd(RS)₂ (for details see [12]).

The insolubility of the precursor is undesirable, because it

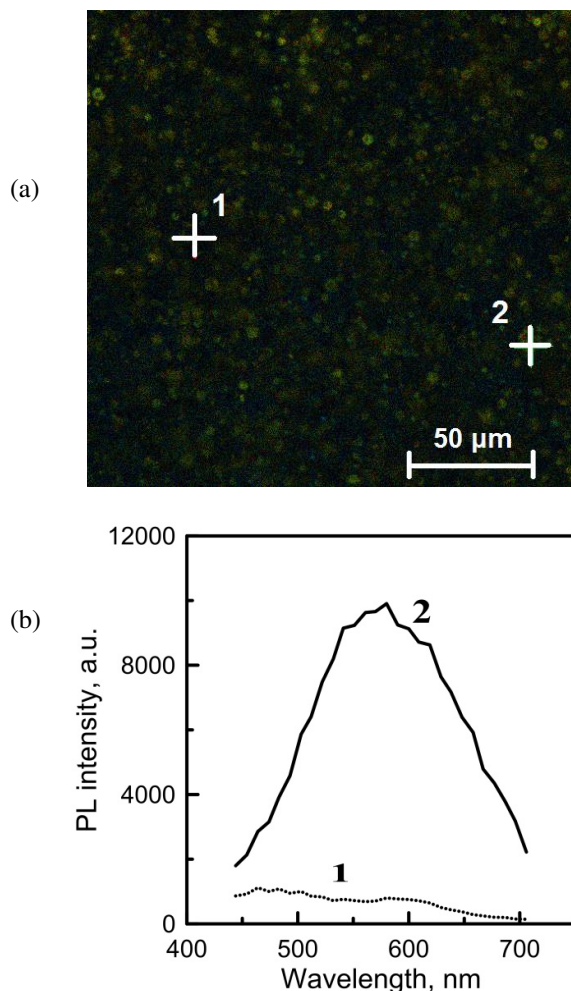


Fig. 4. (a) Photograph of PMMA film with $\text{Cd}(\text{C}_{12}\text{H}_{25}\text{S})_2$ precursor made with fluorescent microscope. The sample was irradiated with pulsed laser at 266 nm. Luminescent islands are seen as green spots. (b) PL spectra taken from different places 1 (out of luminescent island) and 2 (in the luminescent island) (for details see [12]).

III. COMPOSITES WITH SEMICONDUCTOR NANOPARTICLES

There have been several successful attempts to obtain CdS NPs-containing photoinduced nanocomposites with the use of cadmium dithiolates $\text{Cd}(\text{RS})_2$ as precursors [7-10]. Here R is a long alkyl chain or other hydrocarbon ligand. We performed our own investigation with cadmium-(bis)dodecylthiolate ($\text{Cd}(\text{C}_{12}\text{H}_{25}\text{S})_2$) as a precursor and PMMA as a matrix [11]. The fourth harmonic of a Nd:YAG laser (266nm) is suitable for the precursor decomposition, since it has an absorption peak at this wavelength. Samples were prepared by simple casting and by the polymerization technique. The problem with using such kind of compounds as a precursor is that these molecules are practically insoluble in polymer matrices due to the formation of a coordination polymer (Fig. 3) through the intermolecular donor-acceptor interaction [12]. The precursor molecules form islands within the matrix and the CdS NPs are produced just within these islands. It is seen by the fluorescent microscopy of the laser irradiated domains (see Fig. 4a,b) [11,12].

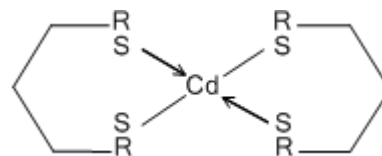


Fig. 5. Schematic view of cyclic complex $\text{Cd}(\text{N}(\text{SCNEt}_2)_2)_2$ (for details see [12]).

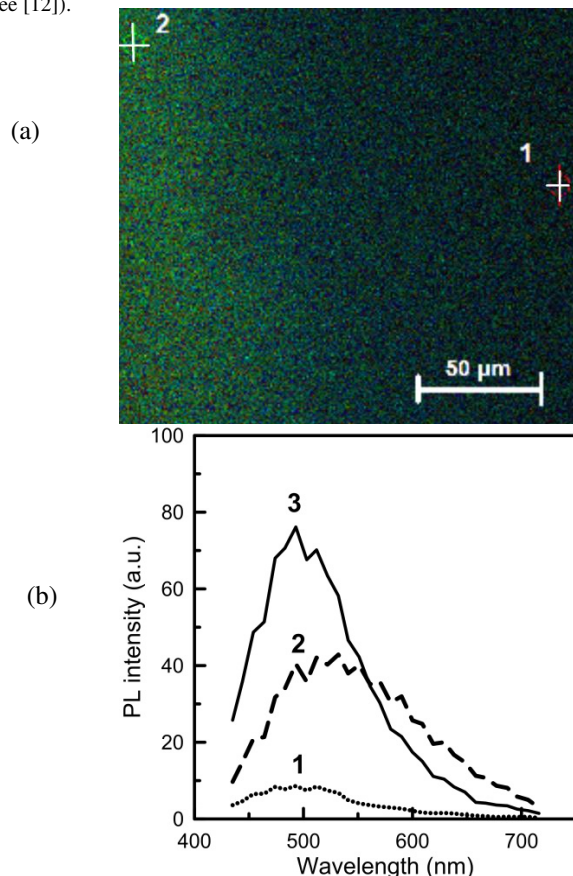


Fig. 6. (a). Fluorescent image of the border between non-irradiated region and region irradiated with UV LED. The sample is PMMA film with 2.5 mass % of $\text{Cd}(\text{N}(\text{SCNEt}_2)_2)_2$ (b). PL spectra taken from non-irradiated area (1), edge of the irradiated area (2), the center of the irradiated region (3). Curves 1 and 2 correspond to the points 1 and 2 at the panel a. (For details see [12]).

hinders the opportunity to control the spatial distribution of the NPs discussed above. It is therefore important to find a soluble precursor for photoinduced creation of semiconducting NPs. Some compounds were suggested in [13,14]. We used bis(1,1,5,5-tetraethyl-2,4-dithiobiureto)cadmium(II), $[\text{Cd}(\text{N}(\text{SCNEt}_2)_2)_2]$ (Fig. 5), synthesized in [15] as a well-soluble in PMMA precursor [12]. The solubility here is better because of the cyclic structure of the compound, so that the intermolecular donor-acceptor interaction is blocked.

Different UV light sources were tried for the irradiation of $[\text{Cd}(\text{N}(\text{SCNEt}_2)_2)_2]/\text{PMMA}$ samples. Here a 266 nm pulsed laser does not seem to be the best choice because of the high absorption and the consequent destruction of the sample. The operating wavelength should be moderately absorbed to modify the sample deeply. The production of high-power UV LEDs (light emitting diodes) is rapidly developing nowadays, and LEDs operating at 365 nm wavelength can be employed for the material modification [16,17]. In paper

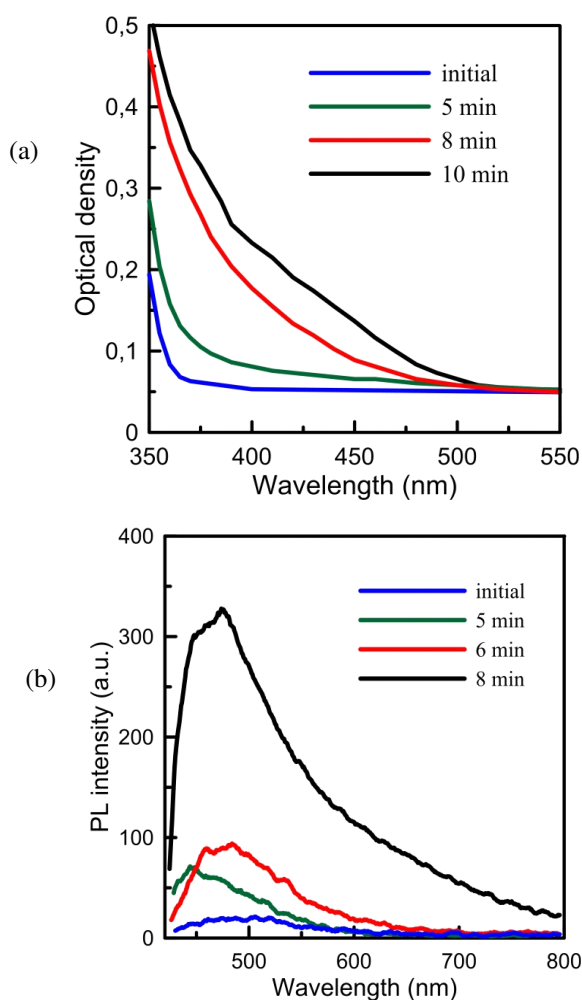


Fig. 7. Change of the optical properties of PMMA film with 1 mass % of $\text{Cd}(\text{N}(\text{SCNET}_2)_2)_2$ after the irradiation with UV LED. The sample was placed close to the LED, so that thermal effect was significant. Curves for different time of irradiation are presented. For details see [12]
 (a) Optical density spectra.
 (b) PL spectra. The excitation wavelength was 405 nm.

[12] we show that UV LED is very good for the effective irradiation of the $[\text{Cd}(\text{N}(\text{SCNET}_2)_2)_2]/\text{PMMA}$ samples. CW irradiation with UV LED simultaneously provides thermal treatment that turns out to be important for the NPs formation. The temperature increases during the irradiation, as well as optical density and PL intensity (Figs. 6-7). The optical properties of the irradiated areas correspond to the formation of CdS particles.

IV. COMPLEX NANOCOMPOSITES

Having in hand soluble precursors for both the plasmon photoinduced nanocomposites and the exciton photoinduced nanocomposites offers an opportunity to obtain more complicated objects such as exciton-plasmon photoinduced nanocomposites containing simultaneously both kinds of precursors and, after irradiation, correspondingly two kinds of NPs within irradiated domains. The interaction between the excited electronic states of semiconductor (exciton) and metal NPs (plasmon) leads to new optical effects [18]. The first attempt of creating the complex photoinduced nanocomposite of such kind was performed in [19]. The pair CdS and Au was chosen because

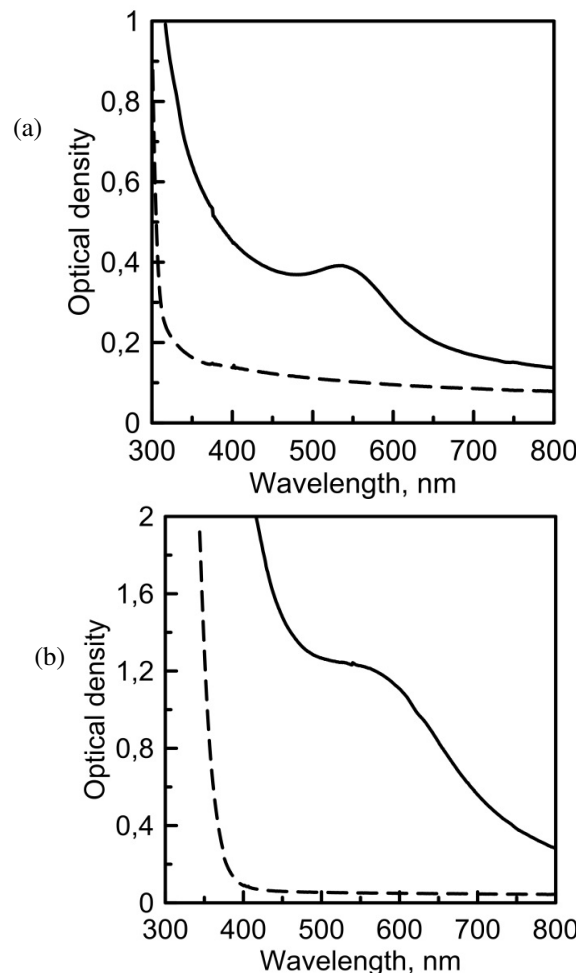


Fig. 8. (a) Optical density of non-irradiated (dashed line) and irradiated with UV LED (solid line) $\text{Ph-C}\equiv\text{C-Au-PPh}_3/\text{PMMA}$ film with the mass fraction of $\text{Ph-C}\equiv\text{C-Au-PPh}_3$ 10%.
 (b) Optical density of non-irradiated (dashed line) and irradiated with UV LED (solid line) PMMA film containing 10 mass % of $\text{Ph-C}\equiv\text{C-Au-PPh}_3$ and 3 mass % of $\text{Cd}(\text{N}(\text{SCNET}_2)_2)_2$ (for details see [19]).

of the overlapping between CdS photoluminescence (PL) band and Au NPs plasmon resonance band.

Both of the precursors added into the PMMA matrix should be soluble. $\text{Cd}(\text{N}(\text{SCNET}_2)_2)_2$ was chosen as CdS precursor. HAuCl_4 and compounds based on it are not compatible with $\text{Cd}(\text{N}(\text{SCNET}_2)_2)_2$.

It was shown in [19] that the gold-containing compound $\text{Ph-C}\equiv\text{C-Au-PPh}_3$ demonstrates the properties of gold precursor. This compound is good soluble in PMMA matrix and gold NPs are formed in $\text{Ph-C}\equiv\text{C-Au-PPh}_3/\text{PMMA}$ samples under effect of LED (365nm) irradiation (Fig. 8a). $\text{Ph-C}\equiv\text{C-Au-PPh}_3$ and $\text{Cd}(\text{N}(\text{SCNET}_2)_2)_2$ can be mixed in PMMA matrix resulting in transparent film containing precursors of two types. After the irradiation by the LED operating at the wavelength of 365 nm, the changes in optical properties (absorption and luminescence spectra) have the signs of the presence of the both kinds of NPs, Au and CdS, within the irradiated domain (Fig. 8b). However, as it was mentioned in [19], we are just at the beginning of the way to obtaining real 3D exciton-plasmon media. The materials involved and irradiation regimes should be improved.

V. CONCLUSIONS

In this small review, we have addressed some achievements and problems in the developing field of direct photoinduced formation of inorganic nanoparticles within the polymer matrix. These nanoparticles tremendously change the optical and mechanical properties of the material. The initiation of the process of the formation of such nanoparticles by light provides an opportunity to obtain complicatedly patterned objects where different parts of the same sample have very different properties. This is promising, for example, for manufacture of complicated photonics structures. It was somehow surprising that powerful UV LED devices appeared to be very useful light sources for processing of photoinduced nanocomposites. Taking into consideration that these devices are relatively cheap, as are the ingredients of the materials involved, one can anticipate that the future development of this field of photoinduced nanocomposites can result in the creation of cheap and reliable nanotechnologies.

REFERENCES

- [1] U. Kreibitz, M. Vollmer, *Optical properties of metal clusters*, Vol. 25, 1993, Springer Series in Materials Sciences, Springer, Berlin.
- [2] D. Bera, L. Qian, T.-K. Tseng, and P.H. Holloway, "Quantum Dots and Their Multimodal Applications: A Review", *Materials*, Vol. 3, 2010, pp. 2260-2345.
- [3] A. Alexandrov, L. Smirnova, N. Yakimovich, N. Sapogova, L. Soustov, A. Kirsanov, and N. Biturin, "UV initiated growth of gold nanoparticles in PMMA matrix", *Appl. Surf. Sci.*, Vol. 248 (1-4), 2005, pp. 181-184.
- [4] N. Biturin, A. Alexandrov, A. Afanasiev, N. Agareva, A. Pikulin, N. Sapogova, L. Soustov, E. Salomatina, E. Gorshkova, N. Tserova, and L. Smirnova, "Photoinduced nanocomposites—creation, modification, linear and nonlinear optical properties", *Appl. Phys. A*, Vol. 112, 2013, pp. 135-138.
- [5] N. Sapogova, and N. Biturin, "Model for UV induced formation of gold nanoparticles in solid polymeric matrices", *Appl. Surf. Sci.*, Vol. 255, 2009, pp. 9613- 9616.
- [6] N. Sapogova, A. Pikulin, A. A. Smirnov and N. Biturin, "Diffusion-controlled alteration of inhomogeneous materials: tailoring of the spatial distribution of nanoparticles in nanocomposites", *Phys.Chem.Chem.Phys.*, Vol. 18, 2016, pp. 32921-32930.
- [7] A. Camposo, M. Polo, A. A. R. Neves, D. Fragouli, L. Persano, S. Molle, A. M. Laera, E. Piscopiello, V. Resta, A. Athanassiou, R. Cingolani, L. Tapfer, and D. Pisignano, "Multi-photon in situ synthesis and patterning of polymer-embedded nanocrystals", *J. Mater. Chem.*, Vol. 22(19), 2012, pp. 9787-9793.
- [8] A. Athanassiou, R. Cingolani, E. Tsiranidou, C. Fotakis, A.M. Laera, E. Piscopiello, and L. Tapfer, "Photon-induced formation of CdS nanocrystals in selected areas of polymer matrices", *Appl. Phys. Lett.*, Vol. 91, 2007, p. 153108.
- [9] D. Fragouli, A.M. Laera, G. Caputo, V. Resta, P.P. Pompa, L. Tapfer, R. Cingolani, and A. Athanassiou, "The effect of polymer matrices in the in-situ CdS formation under UV irradiation of precursor-polymer films", *J. Nanosci. Nanotechnol.*, Vol. 10, 2010, pp. 1267-1272.
- [10] D. Fragouli, V. Resta, P.P. Pompa, A.M. Laera, G. Caputo, L. Tapfer, R. Cingolani, and A. Athanassiou, "Patterned structures of in situ size controlled CdS nanocrystals in a polymer matrix under UV irradiation", *Nanotechnology*, Vol. 20, 2009, p. 155302.
- [11] N. Agareva, A.A. Smirnov, A. Afanasiev, S. Sologubov, A. Markin, E. Salomatina, L. Smirnova, and N. Biturin, "Properties of cadmium-(bis)dodecylthiolate and polymeric composites based on it", *Materials*, Vol. 8, 2015, pp. 8691–8700.
- [12] A.A. Smirnov, A. Afanasiev, N. Ermolaev, and N. Biturin. "LED induced green luminescence in visually transparent PMMA films with CdS precursor", *Opt. Mater. Express*, Vol. 6, 2016, pp.290-295.
- [13] A.K. Bansal, F. Antolini, M.T. Sajjad, L. Stroea, R. Mazzaro, S.G. Ramkumar, K.-J. Kass, S. Allard, U. Scherf, and I.D.W. Samuel. "Photophysical and structural characterization of in situ formed quantum dots", *Phys. Chem. Chem. Phys.*, Vol. 16, 2014, p. 9556.
- [14] L. Stroea, A.K. Bansal, I.D.W. Samuel, S. Kowalski, S. Allard, U. Scherf, L. Ortolani, S. Cavallini, S. Toffanin, and F. Antolini, "Growth of Photoluminescent Cadmium Sulphide Quantum Dots from Soluble Single Source Precursors in Solution and in Film", *Sci. Adv. Mater.*, Vol. 7(1), 2015, pp. 1-14.
- [15] K. Ramasamy, M. A. Malik, M. Helliwell, J. Raftery, and P. O'Brien, "Thio- and dithio-biuret precursors for zinc sulfide, cadmium sulfide, and zinc cadmium sulfide thin films", *Chem. Mater.*, Vol. 23, 2011, pp. 1471–1481.
- [16] NICHIA LED Catalogue October 2017 Release. Available: http://www.nichia.co.jp/specification/catalogue/2017_02/NICHIA_LED_Catalogue2017_02_05.pdf
- [17] K. Hölz, J. Lietard, and M.M. Somoza, "High-power 365 nm UV LED mercury arc lamp replacement for photochemistry and chemical photolithography", *ACS Sustain. Chem. Eng.*, Vol. 5(1), 2017, pp. 828-834.
- [18] J.-B. Li, M.-D. He, and L.-Q. Chen, "Four-wave parametric amplification in semiconductor quantum dot-metallic nanoparticle hybrid molecules", *Opt. Express*, Vol. 22, 2014, p. 24734.
- [19] N. Biturin, N. Ermolaev, A.A. Smirnov, A. Afanasiev, N. Agareva, T. Koryukina, V. Bredikhin, V. Kamenskiy, A. Pikulin, and N. Sapogova. "Plasmonic, excitonic and exciton-plasmonic photoinduced nanocomposites", *Appl. Phys. A*, Vol. 122, 2016, p. 193.

Anton A. Smirnov is junior researcher in the Laboratory of Laser Nanomodification of Materials in the Institute of Applied Physics of the Russian Academy of Sciences. He obtained his Master of Science degree in solid-state physics, Advanced School of General and Applied Physics of Lobachevsky State University, Nizhny Novgorod, Russia in 2013. Research interests are light-matter interaction, photo-induced processes and physics of nanostructures.

Andrey Afanasiev is a researcher in the Laboratory of Laser Nanomodification of Materials in the Institute of Applied Physics of the Russian Academy of Sciences. He obtained his Master of Science degree in physics, Advanced School of General and Applied Physics of Lobachevsky State University, Nizhny Novgorod, Russia in 2001. Research interests are nonlinear optics, photo-induced processes and physics of nanostructures.

Nikita Biturin was born in Nizhny Novgorod (Gorky), Russia, in 1954. He graduated from Nizhny Novgorod State University in 1977, and received his Ph.D. and Dr. Sci. degrees from Institute of Applied Physics Russian Academy of Sciences (IAP RAS). Since 2012, he is Professor in Laser physics according to 'Highest Attestation Commission' at the Ministry of Education and Science of Russian Federation (VAK). He has been with IAP RAS since 1977. Since 1993, he worked also as an Invited Researcher at Johannes Kepler University, Linz, Austria, LPL and LIMHP CNRS Laboratories, Villetaneuse, France, Data Storage Institute, Singapore, and as an Invited Professor at University Paris-Nord, France. His scientific interest is laser-matter interaction including laser effects on polymers, biological tissues and sol-gel materials. He is the Head of Laboratory for Laser Nanomodification of Materials at IAP RAS.