ISSN 1070-3632, Russian Journal of General Chemistry, 2013, Vol. 83, No. 11, pp. 2195–2202. © Pleiades Publishing, Ltd., 2013.
Original Russian Text © G.E. Adamov, K.S. Levchenko, V.R. Kurbangaleev, P.S. Shmelin, E.P. Grebennikov, 2012, published in Rossiiskii Khimicheskii Zhurnal, 2012, Vol. 56, Nos. 1–2, pp. 76–82.

Functional Hybrid Nanostructures for Nanophotonics: Synthesis, Properties, and Application

G. E. Adamov, K. S. Levchenko, V. R. Kurbangaleev, P. S. Shmelin, and E. P. Grebennikov

Tekhnomash Central Research Institute of Technology, ul. Ivana Franko 4, Moscow, 121108 Russia
e-mail: ntc_technology@socket.ru

Received June 1, 2012

Abstract—The review considers the potential of hybrid nanostructures in creating smart materials with optically controlled properties. The goals and technologies of development of stable hybrid nanostructures are analyzed. Some experimental results concerning smart materials with optically controlled properties, including those based on a unique photochromic material bacteriorhodopsin, which have a great potential in the development of a new type information systems, are summarized.

DOI: 10.1134/S107036321311039X

The progress of modern technologies is impossible to imagine without the development of new materials, including those based on hybrid structures. Hybrid structures constructed of organic compounds and including inorganic components have finely tunable physicochemical parameters, which extends their application field (solar cells [1, 2], organic light emitting diodes [3], UV sensors [4–6], photo-chromic glasses [7–11], thermochromic glasses [11], photon-driven nanomachines [12], efficient catalysis [13, 14], biosensors [15, 16], and medicine [17–19]).

In the present review we consider the hybrid nanostructures relevant to smart materials with controlled spectral characteristics.

The possibility of application of hybrid nanostructures in photonics is based on the ability of nanoobjects to affect the lifetime of excited states of atoms and molecules which are remote from each other at distances shorter than the exciting wavelength [20]. This effect depends on the distance of the components of hybrid structures from each other and on their mutual arrangement, and it sharply enhances in the vicinity of nanoparticles in cases where strong electromagnetic fields localize at the plasmon resonance frequency [21]. Strong local fields affect the rate of electronic transitions, i.e. on the lifetime of excited states, and they can affect light absorption and radiation parameters, energy (photo or electrical) transfer, as well as much enhance various nonlinear optical effects.

In a general case, a hybrid nanostructure is a system of nanoparticles of different natures (metal colloid nanoparticles, semiconductor quantum dots, oxide or polymer nanoparticles, etc.) and functional molecules (photochromic, photoluminescent, electroluminescent, magnetically active, etc.) (Fig. 1). Hybrid nanostructures can also include auxiliary substances (spacers).

As mentioned above, the mutual effect of nanoobjects is much dependent on the distance between them, and this distance can be varied by means of spacers with different linear dimensions. Thus, a spacer with a definite geometry can define the physicochemical parameters of the hybrid structure as a whole. Materials with dynamically controlled properties can be created using photo-, electro-, thermo-, and pH-sensitive substances as spacers. For example, photochromic molecules capable of changing their linear dimensions under light irradiation were proposed as spacers [22, 23].

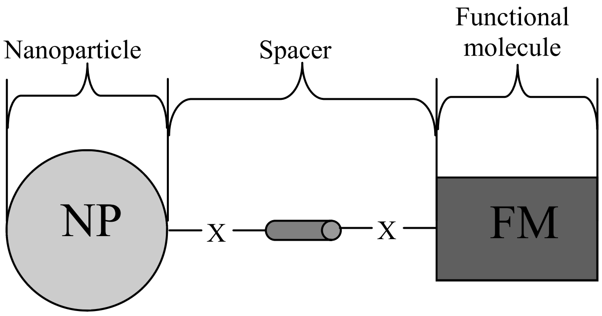

Fig. 1. Schematic presentation of a hybrid nanostructure.

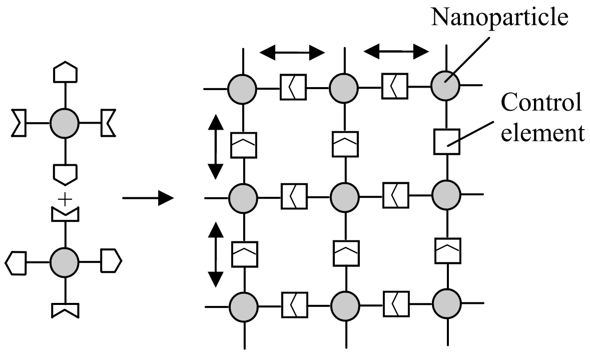

Fig. 2. Schematic presentation of 3D structures comprising nanoparticles and control elements.

Hybrid nanostructures can form 3D ordered or fractal systems (X-dimensional nanostructures, threads, or dendrimers [24], multilayer structures [25]) with dynamically controlled properties (Fig. 2).

Developing of hybrid nanostructures one should solve a number of tasks: to synthesize and stabilize nanoparticles, to functionalize their surface, to synthesize spacers and functional molecules with desired properties, to link functional molecules to the nanoparticle surface, and to ensure functionality and stability of molecules comprised in hybrid structures and stability of hybrid nanostructures as a whole.

Synthesis, stabilization, and functionalization of nanoparticles. By now a number methods of synthesis and stabilization of nanoparticles of different nature have been developed [26–28]. The most common stabilizers are organic compounds with a high affinity to the nanoparticle surface. For example, alkanethiols are used to stabilize metal nanoparticles [29], and trioctylphoshine oxide and stearic acid are tradinital stabilizers for quantum dots [30, 31]. However, not all stable nanoparticles are suitable to create of hybrid nanostructures. First of all this depends on the nature of the stabilizer molecule. An important criterion of the feasibility of nanoparticles for constructing hybrid nanostructures is the possibility of replacement of stabilizer molecules by spacers. This process is referred to as surface functionalization of nanoparticles. A specific procedure of surface functionalization involves consecutive introduction of several spacers which link to each other and thereby affect the physicochemical nature of the initially functionalized nanoparticle surface [32]. One of the most practical approaches to functionalized nanoparticles is introduction of spacer molecules at the stage of nanoparticle synthesis, and, therewith, the spacers function as stabilizers [33].

Structural features of spacers. For a compound to work as a spacer, it should include at least two substituents to link it both to the surface of nanoparticles and to the functional molecule. Linking can be due to van der Waals interactions, hydrogen bonding, ionic and affine interactions, covalent bonding, and complex formation; moreover, several binding mechanisms can be involved. Low-molecular compounds are best bound to the surface of an inorganic material by substituents prone to covalent, affine, electrostatic, or ionic interactions. Substituents of different nature may provide selective linking, if, for example, one of them interacts with nanoparticles and the other, with the functional molecule [34]. Such an approach forms the basis of self-organization of structures.

Requirements to functional molecules for hybrid nanostructures. The main task to be solved in the synthesis of functional molecules is to introduce in their structure such substituents that can provide linking to the nanoparticle surface. Substituents are chosen in view of the physicochemical features of the nanoparticle surface, specifically, whether it is functionalized by spacers or not. For example, if the nanoparticle surface is functionalized by carboxy groups, the substituent of choice in the functional molecule may be amino groups. Sometimes functional molecules already contain groups capable of linking to the nanoparticle surface. Such molecules usually cross-link to nanoparticles by the exchange mechanism: One or several stabilizer molecules are replaced by an organic functional molecule [35, 36].

Linking functional molecules to nanoparticle surface. Depending on the nature of the nanoparticles, different requirements are placed to substituents responsible for linking. In the case of metal and semiconductor nanoparticles, functional groups should be capable of forming strong bonds with transition metals which are the key component of such nanoparticles. The strongest linking is provided by thiol groups (R–SH, where R = alkyl, aryl) which competitively replace stabilizer molecules. An alternative for thiols as linkers in constructing hybrid nanostructures are disulfides RSSR [35]. Slightly weaker linking agents are sulfides (dialkyl sulfides [37] or alkyl aryl sulfides [38]), as well as thioamides. The popular linkers are phenolic (ArO^-) [39], carboxy

($RCOO^-$), sulfo (RSO_3^-), and phosphate groups ($R_xPO_y^{z-}$) [40]. However, stability of such particles are not infrequently limited by ions which are present in the surrounding medium and are capable of competitively substituting the linked molecules, thus destroying the hybrid nanostructure.

Retention of properties of functional molecules incorporated into hybrid nanostructures. Sometimes molecules incorporated in hybrid nanostructures lose their functional properties. Thus, Sidhaye et al. [41] showed that in hybrid nanostructures comprising gold nanoparticles and an azobenzene nanochromic compound, light-induced isomerization of azobenzene, which needs a lot of free space, is strongly hindered due to a dense packing of chromophoric centers on the surface of nanoparticles. This hindrance can be eliminated by introducing additional auxiliary compounds which link with nanoparticles and separate chromophores (for example, alkyl- and/or arylamines, such as *n*-octylamine [42], benzyldimethylstearylammonium bromide [41]).

Stability of hybrid nanostructures. Stability of a hybrid nanostructure and retention of its functions depend on a number of factors, among which the strength of linking of the organic and inorganic components, resistance of the organic component to external stresses, and molecular environment deserve mentioning. Methods to protect hybrid nanostructures from contact with foreign low-molecular compounds have been developed, for example, encapsulation and linking. Encapsulation consists in the coating of hybrid structures with silicate materials: polymers, polypeptides, phospholipids, polysaccharides, etc. [43, 44].

Linking is more appropriate for protecting polyfunctional organic molecules residing on the surface of a hybrid nanostructure. In this case, isolation is performed by treatment of the hybrid nanostructure with a difunctional reagent, for example, glutaraldehyde which reacts by both its aldehyde groups with active centers in the polyfunctional hybrid structure [45]. An isolated hybrid nanostructure retains its useful property (plasmon resonance, magnetism, catalytic activity, etc.) and acquires such additional properties as biocompatibility with living systems, solubility in polar and apolar solvents, resistance to aggressive media, etc. For example, hybrid nanostructures comprising semiconductor nanoparticles and organic fluorophores hold great promise as a basis for producing novel fluorescent probes for biological and medical applications [15]. Semiconductor nanoparticles based on Cd-chalcogenides are highly toxic for living organisms, but being encapsulated into biocompatible films or proteins, they exert no toxic effects on live cells. Hybrid nanostructures on the basis of quantum dots and fluorophores are encapsulated by linking with 1-ethyl-3-[3-(dimethylamino)propyl]carbodiimide hydrochloride [46]; affine binding of biotin to stretavidin has also been reported [47] (bridging avidin molecules [48]) or self-assembly processes [49] are frequently used instead of stretavidin).

Evidence is available for a enhancement stability of components in certain hybrid nanostructures, for example, in hybrid nanostructures on the basis of enzymes immobilized on the surface of silicon dioxide nanospheres. Lee et al. showed [50] that penicillin-G acylase (an enzyme cleaving penicillin-G into 6-aminopinicillane and phenylacetic acids) covalently bond in a hybrid nanostructure preserves 72% of its initial activity after 10 catalytic cycles. Enzymes in hybrid structures show enhanced stability in acidic and alkaline media, and their globular structure is not destroyed at high temperatures [51].

Ways to enhance resistance of hybrid systems to specific factors are generally determined experimentally by searching for compounds for strengthening or replacement of weak components in the hybrid structure.

Polyaggregation of nanoparticles as a way to construct new materials. As mentioned above, the distance between the nanoparticle and functional molecule in a hybrid structure is an important factor responsible for the properties of the hybrid structure. At the same time, of no little importance for the properties of the material as a whole is the mutual arrangement of the nanostructures in the material. They can locate at arbitrary distances from one another and also self-aggregate to form polyaggregates, clusters, and multilayer structures [52, 53].

The type of aggregation depends on many factors, including concentration, shape and size of nanoparticles, nature of the functionalized surface (length of spacers and their steric structure and presence of active groups), or molecular environment [54]. For example, rod-shaped gold nanoparticles have a nonuniform charge distribution on the surface and, due to this, they are capable of forming thread-like structures in the presence of bifunctional stabilizer spacers (1-phenyl-1,2-ethanedithiol or 1,2-ethanedithiol) [55].

Spherical structures characteristically form 3D dendrimer or honeycomb structures [24]. Clear evidence was obtained that the type of aggregation and distance between the nanostructures in such materials determine the spectral properties of the material. For example, magnetic spherical nanoparticles of a preset diameter, which are functionalized by spacers on the basis of dendritic polyamide amine molecules with different linear dimensions, form polyaggregates. Therewith, their absorption range is directly related to the nanostructure–nanostructure distance preset by the spacers.

Dynamic control of the spectral properties of such structures is possible by means of a light-controlled spacer. For example, Sidhaye et al. [41] proposed an approach to forming hybrid nanostructures comprising gold nanoparticles and an azobenzene photochromic substance. Azobenzene and nanoparticles are linked using a specially synthesized protein molecule with two end cysteine-based residues. One azobenzene molecule cross-links two nanoparticles, which leads to formation of a continuous network of bonds between all nanoparticles present in the bulk material. Under UV irradiation the azobenzene molecules undergo *trans-cis* isomerization, which reduces the distance between nanoparticles from ~3 to ~2 nm.

Hybrid nanostructures for materials with controlled spectral properties. The influence of nano-objects on the lifetime of the excited states of functional molecules present of the surface of the nano-object, which may result in that the spectral characteristics of hybrid nanostructures get quite different from the spectral characteristics of their individual components. For example, controlled luminescence enhancement or suppression, radiationless energy transfer between the nanostructure components, and control of the quantum yields of photochromic reactions and lifetimes of intermediate excited states may prove possible. Below we present the experimental results providing evidence for this suggestion.

Hybrid nanostructures basid on polymers with π-conjugated bonds and metal nanoparticles characteristically exhibit enhanced luminescence. Thus, the luminescence intensity of the hybrid structure comprising polythiophene nanorods with a metal (copper, nickel, or cobalt) nanocoating is 25–100 times stronger compared with that of usual polythiophene nanotubes [58]. Therewith, the luminescence peak shape also changes. If unmodified polythiophene nanotubes give three narrow bands (half-width $\leq$ 10 nm) with their maxima at 525, 580, and 625 nm and a weak halo at 500–750 nm, modified nanotubes gave a broad luminescence band comprising at least two unresolved bands with their maxima at 630 and 670 nm. The change of the luminescence spectrum gives grounds to suggest that the luminescence mechanism of the hybrid structure is sharply affected by nanoparticles. The limunescence intensity of a similar structure on the basis of poly[2-methoxy-5-(2'-ethylhexyloxy)-*p*-phenylenevinylene] and gold nanoparticles is enhanced 30 times [57]. Therewith, the luminescence maximum is shifted from 560 to 548 nm, while its shape remains unchanged.

Grebennikov [58] studied the absorption and luminescence spectra of suspensions of hybrid structures comprising CdSe/ZnS semiconductor nanoparticles and a phenalenone flurophore. As shown, the absorption spectra of the CdSe/ZnS hybrid nanostructures with the core diameter d_{CdSe} of 2.5 nm (emission wavelength $\lambda_e = 530\pm5$ nm) over the entire measured spectral range (300–700 nm) provide evidence for the optical clarification of the suspension. By contrast, the absorption spectra of the CdSe/ZnS hybrid nanostructures with the core diameter d_{CdSe} of 3.5 ($\lambda_e = 560\pm5$ nm) over the entire measured spectral range (300–700 nm) demonstrate an increase of the optical density of the suspension. In the first case, the linear absorption coefficient is lower by 46%, while in the second, it is higher by 100% of the sum of the linear absorption coefficients of the individual components of the structure at equivalent concentrations. At the same time, the luminescence spectra of the CdSe/ZnS hybrid nanostructures with d_{CdSe}=2.5 nm and $\lambda_e = 530\pm5$ nm at $\lambda_{ex} = 375$ nm show a ≈1.5-fold lower luminescence at $\lambda_e = 530$ nm. By contrast, the luminescence spectra of the CdSe/ZnS hybrid nanostructures with $d_{\mathrm{CdSe}} =$ 3.5 nm and $\lambda_e = 560\pm5$ nm at $\lambda_{ex} = 530$ nm show a ≈20% higher luminescence at $\lambda_e = 570$ nm.

In [58], the authors also studied reversible light-managed variation of the luminescence intensity of dihetaryl–phenalenone CdSe/ZnS hybrid nanostructure. To this end, hybrid structures on the basis of CdSe/ZnS semiconductor nanoparticles and phe-nalenone with a dihetarylethene photochromic spacer were synthesized and studied. The luminescence intensity of the CdSe/ZnS hybrid nanostructures both with $d_{\mathrm{CdSe}} =$ 3.5 nm and $d_{\mathrm{CdSe}} = 2.5$ nm could be reversibly light-controlled (by 10% and 75%, respec-tively) on alternate irradiation with UV light (≈7 mW cm^{-2}) and the light with

λ= 532 nm ($\approx$200 mW cm^{-2}), which induce a photochromic transition in the dihetarylethene molecule.

Luo et al. [59] described the results of research on the properties of a hybrid structure comprising gold nano-particles coated with thermosensitive poly(*N*-isopropylacrylamide) with covalently bound substituted azobenzene residues. The nanoparticle surface was modified by α-cyclodextrin to provide host–guest binding with azobenzene. Under UV irradiation azobenzene undergoes *trans–cis* isomerization which is accompanied by changes in the linear dimensions of the molecule. However, the *cis* form of azobenzene is incapable of complex formation with α-cyclodextrin, and the hybrid structure is destroyed. The reverse *cis–trans* isomerization takes place under irradiation at $\lambda >$ 420 nm. This, by exposure of the azobenzene residues to light one can control the optical properties of the material. Another way to control the optical properties of this hybrid nanostructure is based on exposure to heat, since poly-(*N*-isopropylacrylamide) is a thermosensitive polymer. Increasing temperature induces a phase transition accompanied by the formation of a globular polymer structure (according to dynamic light scattering measurements, the particle size changes from 40 nm at 25°C to 620 nm at 35°C). Therewith, the transmittance at 750 nm sharply changes: from 95% to almost zero. This process is cyclic and reversible.

Bacteriorhodopsin as a functional component of hybrid nanostructures. Hybrid nanostructures suitable for creating spectrally controlled materials should include photoactive molecules. Among the diversity of photochromic, fluorescent, and other photoactive compounds, a particular place belongs to a unique biological material bacteriorhodopsin (bR) [60]. This supersensitive protein similar to the human visual pigment rhodopsin was detected in halobacteria, where it is built in cellular membranes (so-called purple membranes). In the membrane it is present as a trimer whose characteristic size (diameter) is about 10 nm. The purple membranes isolated from bacterial cells completely retain their structure.

In a live cell, bR trophic function is light-dependent transmembrane proton transport. Systems based on bR behave as photochromic and photoelectric materials featuring high cyclicity (>10^6) and optical resolution (~5000 lines/mm) [61], as well as a unique stability. They retain their properties in suspensions and films for a long time (longer than 10 years) [61, 62].

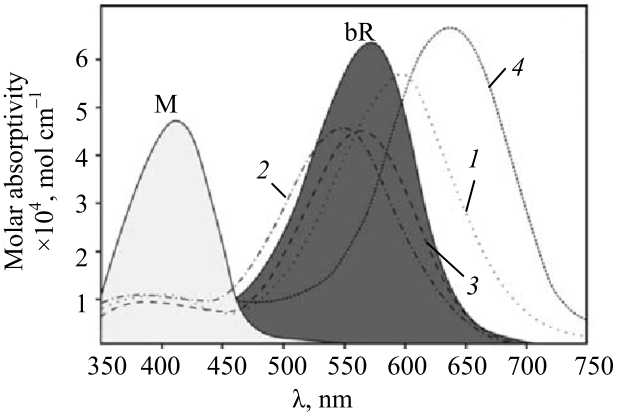

Fig. 3. Absorption spectrum of bacteriorhodopsin and basic photocycle intermediates (*1*) K, (*2*) L, (*3*) N, and (*4*) O.

The photochromic properties of bR are defined by the photochemical cycle. Having absorbed light quantum, its molecules pass sequential states (intermediates) and spontaneously return to the ground state [63]. Therewith, cyclic changes of optical characteristics (reflection and absorption coefficients) occur [64]. Note that the principal light-induced cycle of bR involves six intermediates, and each intermediate is identified by the absorption spectrum (Fig. 3). The absorption maxima of the ground state bR570 and long-lived light-induced state M412 are distant from each other by ~150 nm.

Bacteriorhodopsin-based materials have quite a broad potential application field. These are optical devices for information processing [65, 66] and storage [67], recording dynamic holograms [68], space–time light modulators [69], technical vision systems [70], etc. An interesting field is the development of photoreceptors including bR-containing materials and other photochromic compounds, which have a broader range of spectral sensitivity [71].

It is suggested that the potential of bR can be best realized in hybrid nanostructures [60].

Hybrid nanostructures on the basis of bacteriorhodopsin. Adamov et al. [72] synthesized hybrid structures comprising silver nanoparticles and bacteriorhodopsin with cysteine, arginine, lysine, and polylysine as spacers. In the spectra of suspensions of the hybrid nanostructures including lysine and polylysine, the absorption maxima of silver nanoparticles are shifted from 391 to 405 nm and from 398 to 403 nm, respectively. In the case of cysteine as a spacer, the absorption maxima of Ag nanoparticles and bR are not shifted. These findings can be explained by the different distances between the components of the nanostructures (~0.4 nm with cysteine, ~0.8 nm with lysine, and ~1.4 nm with polylysine). Evidence for the mutual effect of the components of the hybrid nanostructures comes from the intensity enhancement of absorption maxima for Ag by 8–10% (polylysine) and 13–15% (cysteine) and for bR by 4–6% (polylysine) and 24–26% (cysteine) as compared with the values obtained by simple summation of the spectra of the individual components at the same concentrations. It was found that nanoparticles incorporated in a hybrid nanostructure sharply enhance the effect of compounds which affect the bR photocycle. This gives additional opportunities to control the efficiency of light-induced reactions and the lifetime of spectral intermediates. The introduction of silicates $(Na,K)_2SiO_{3-x}$ in concentrations of 2×10^{-5}–7×10^{-4} wt % into a suspension of hybrid nanostructures (Ag–polylysine–bR, Ag : bR weight ratio 1 : 5) radically changes the spectrum and relative fractions of spectral intermediates (M412 becomes a prevailing form): The hybrid structure changes color from reddish violet to yellow.

Approaches to the creation of elements of organic solar cells by the principle of Grätzel cells, with titanium oxide replaced by semiconductor quantum dots and bR used as a photosensitizer, were proposed in [73–75]. Hybrid structures were synthesized by self-assembly on the purple membrane surface of quantum dots coated by thioglycolic acid. Quantum dots and bR were linked by means of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide, which provided the separation distance between the nanoparticle core surface and retinal, the bR chromophore center, of about 3–5 nm. The other technology used in the cited work was biotin–streptavidin affine binding to achieve a 7–9-nm nanoparticle–bR retinal separation distance. Luminescence of quantum dots in such structures is suppressed, and the transferred energy is used to induce a photochromic transition in bR, which increases the quantum yield of the bR photoreaction several times.

At present essential practical results providing evidence for the scientific significance and engineering potential of hybrid nanostructures have been obtained. The development of a theoretical background and methods of modeling for a deeper insight into the mechanism of mutual effect of the components of hybrid nanostructures and prediction of their properties would contribute much into the progress of this field.

Enhancement of the stability and efficiency of nanostructures still remains the most important tasks in the field of their development and practical application. This tasks can be solved in different ways depending on the desired application of the materials to be developed. For example, development of isolation technologies holds the greatest promise for constructing hybrid nanostructures for high-efficiency drugs and their targeted delivery, as well as for imparting to such drugs a higher stability in the living body.

At the same time, a solution for nanophotonic applications (organic solar cells and light diodes, fluorescent optical memory, etc.) might consist in forming functional materials with the electronic conductivity, quantum yields of light-induced and fluorescence reactions, and other characteristics enhanced due to an ordered arrangement of hybrid nanostructures (3D clusters, polyaggregates, threads, dendrimers).

In view of the intensity and diversity of the R&D works on the synthesis of novel functional compounds, as well as the possibility for synthesizing nanoparticles of different geometries and compositions, one should expect that the technologies of construction of hybrid nanostructures will long remain one of the strategic lines of development of radically new functional materials.

REFERENCES

1. Ferreira, S.R. et al., *Organic Electronics*, 2011, vol. 12, no. 7, pp. 1258–1263.
2. Saunders, B.R., *J. Coll. Int. Sci.*, 2012, vol. 369, no. 1, pp. 1–15.
3. Rizzo, A. et al., *Proc. of SPIE*, 2008, vol. 6910, pp. 69100O-69100O-8.
4. Chambers, J.P. et al., *Curr. Issues Mol. Biol.*, 2008, vol. 10, pp. 1–12.
5. Barhoumi, A.H. et al., *Mater. Sci. Eng. C*, 2006, vol. 26, pp. 328–333.
6. Zong, Sh., *Anal. Lett.*, 2007, vol. 40, pp. 1556–1568.
7. Volkan, M., et al., *Sens. Actuators, B*, 2005, vol. 106, p. 660.
8. Tang, Y.K. et al., *Advanced Sensor Systems and Applications II, Proc. SPIE*, 2005, vol. 5634, p. 669.
9. Xu, H. et al., *Chem. Mater.*, 2007, vol. 9, pp. 2489–2494.

10. Herrikhuyzen, J. et al., *ACS Nano*, 2010, vol. 4, no. 11, pp. 6501–6508.
11. Pardo, R. et al., *Chem. Soc. Rev.*, 2011, vol. 40, pp. 672–687.
12. Carroll, G.T. et al., *Chem. Sci.*, 2010, vol. 1, pp. 97–101.
13. Kang, Y. et al., *J. Mater. Chem.*, 2011, vol. 21, pp. 3704–3710.
14. Lee, Ch. et al., *Nano Today*, 2009, vol. 4, pp. 165–179.
15. Mattoussi, H. et al., *Adv. Drug Delivery Rev.*, 2012, vol. 64, vol. 2, pp. 138–166.
16. Heller, A., *Annu. Rev. Biomed. Eng.,* 1999, vol. 1, pp. 153–175.
17. Decraenea, V., *Curr. Nanosci.*, 2009, vol. 5, pp. 257–261.
18. Gibson, J.D., et al., *J. Am. Chem. Soc.*, 2007, vol. 129, pp. 11653–11661.
19. Wu, W., *Biomaterials,* 2010, vol. 31, pp. 7555–7566.
20. Klimov, V., *Nanoplasmonics: Fundamentals and Applications*, Singapore: PanStanford Publishing, 2012.
21. Klimov, V.V., Ducloy, M., and Letokhov, V.S., *Quantum Electronics,* 2001, vol. 31, no. 7, pp. 569–586.
22. Grebennikov, P.P., RF Patent no. 2007109454, 27.08.2008.
23. Grebennikov, P.P. et al., RF Patent no. 2007109453, 27.08.2008.
24. Pyun, J., *Polymer Rev.*, 2007, vol. 47, pp. 231–263.
25. Yuan, B. et al., *Nanotechnology*, 2011, vol. 22, p. 315303.
26. Dykman, L.A. and Bogatyrev, V.A., *Russ. Chem. Rev.*, 2007, vol. 76, no. 2, p. 181.
27. Krutyakov, Yu.A. Kudrinskiy, A.A., Olenin, A.Yu., and Lisichkin, G.V., *Russ. Chem. Rev.*, 2008, vol. 77, no. 3, p. 233.
28. Bera, D. et al., *Materials,* 2010, vol. 3, no. 4, pp. 2260–2345.
29. Brust, M., et al., *J. Chem. Soc., Chem. Commun.*, 1994, no. 7, pp. 801–803.
30. Hines, M.A. and Guyot-Sionnest, P., *J. Phys. Chem., B.*, 1996, vol. 100, no. 2, pp. 468–471.
31. Qu, L. et al., *Nano Lett.,* 2001, vol. 1, pp. 333–337.
32. Grebennikov, E.P. and Adamov, G.E., RF Patent no. 2007146615/15, 20.09.2009.
33. Grebennikov, E.P., Malyshev, P.B., Shmelin, P.S., and Adamov, G.E., *Nanoinzheneriya*, 2011, no. 6, pp. 29–34.
34. Lowe, C.R., *Curr. Opin. Struc. Biol.*, 2000, vol. 10, no. 1, pp. 428–434.
35. Rudakovskaya, P.G., *Mendeleev Commun.*, 2010, vol. 20, pp. 158–160.
36. Schulz-Dobrick, M. et al., *J. Am. Chem. Soc.*, 2005, vol. 127, pp. 12816–12817.
37. Vázquez, M.J.R. et al., *Nanomaterials for Application in Medicine and Biology*, Giersing, M. and Khomutov, G.B., Eds., Bonn: Springer, 2008, pp. 114–125.
38. Peterle, T. et al., *Chem. Commun.*, 2008, pp. 3438–3440.
39. De, M. et al., *Adv. Mater.*, 2008, vol. 20, pp. 4225–4241.
40. Neouze, M.-A. et al., *Monatsh Chem.*, 2008, vol. 139, pp. 183–195.
41. Sidhaye, D.S. et al., *Langmuir*, 2005, vol. 21, pp. 7979–7984.
42. Misami, R. et al., *Angewandte Chemie, Int. Ed.,* 2004, vol. 43, pp. 6135–6139.
43. Luo, Sh. et al., *J. Phys. Chem. B,* 2005, vol. 109, pp. 22159–22166.
44. Zhang, L. and Zhang, L., *Nano LIFE*, 2010, vol. 1, pp. 163–173.
45. Zhao, B., Shi, B., and Ma, R., *Eng. Life Sci.*, 2005, vol. 5, pp. 436–441.
46. Susumu, K. et al., *J. Am. Chem. Soc.*, 2007, vol. 129, pp. 13987–13996.
47. Lidke, D.S. et al., *Nat. Biotech.*, 2004, vol. 22, pp. 198–203.
48. Zhang, C.Y. et al., *Nat. Mater.,* 2005, vol. 4, pp. 826–831.
49. Poselt, E. et al., *Langmuir*, 2009, vol. 25, pp. 13906–13913.
50. Lü, Y. et al., *Adv. Funct. Mater.*, 2007, vol. 17, pp. 2160–2166.
51. Lee Ch.-H. et al., *Nano Today*, 2009, vol. 4, pp. 165–179.
52. Chapel, J.-P. and Berret, J.-F., *Curr. Opin. Colloid In.*, 2012, vol. 17, pp. 97–105.
53. Peterle, T., *Adv. Funct. Mater.*, 2009, vol. 19, pp. 3497–3506.
54. Lee, G., *Korean J. Chem. Eng.*, 2011, vol. 28, no. 8, pp. 1641–1650.
55. Tomas, K.G., *Curr. Trends Sci.*, 2009, pp. 53–66.
56. Joo, J. et al., *Adv. Mater.*, 2007, vol. 19, pp. 2824–2829.
57. Kim, M.S. et al., *ACS Nano*, 2009, vol. 3, no. 6, pp. 1329–1334.
58. Grebennikov, E.P., *Doctoral (Tech.) Dissertation*, Moscow, 2010.
59. Luo, C. et al., *Macromol. Rapid Commun.*, 2008, vol. 29, pp. 149–154.
60. Adamov, G.E. et al., *J. Photochem. Photobiol. A: Chem.*, 2008, vol. 96, nos. 2–3, pp. 254–261.
61. Hampp, N., *Chem. Rev.*, 2000, vol. 100, pp. 1755–1776.
62. Vsevolodov, N.N., *Pigmenty–fotoregistratory* (Pigments–Photorecorders), Moscow: Nauka, 1988.
63. Haupts, U. et al., *Ann. Rev. Bioph. Biomol.*, 1999, vol. 28, pp. 367–399.
64. Zeisel, D. and Hampp, N., *J. Phys. Chem.*, 1992, vol. 96(19), pp. 7787–7792.

65. Thoma, R. et al., *Opt. Lett*., 1991, vol. 16(9), pp. 651–653.
66. Downie, J.D., *Appl. Optics*, 1995, vol. 34(23), pp. 5210–5217.
67. Birge, R.R. et al., *Mol. Cryst. Liq. Cryst. B*, 1992, vol. 3, pp. 133–148.
68. Fitzpatrick, C. et al., *Opt. Eng.,* 1998, vol. 37(6), pp. 1708–1713.
69. Imam, H. et al., *Opt. Lett*., 1995, vol. 20(2), pp. 225–227.
70. Goldobin, I.S. et al., *Syst. Sredstva Svyazi, Televid. i Radioveshch*., 2002, nos. 1–2, pp. 56–63.
71. Choi, H.-G. et al., *Biosens. Bioelectron.*, 1998, vol. 13, pp. 1069–1075.
72. Adamov, G.E. et al., *Collected Papers of XIV Mezhdunaridnaya. nauchno-tekhnicheskaya. konf. "Vysokie tekhnologii v promyshlennosti Rossii"* (XIV Sci. and Tech. Conf. "High Technology in Russian Industry"), Moscow: Tekhnomash, 2008, pp. 151–154 .
73. Rakovich, A. et al., *Proc. SPIE*, 2009, vol. 7366, pp. 736620-1–736620-8.
74. Rakovich, A. et al., *Nano Lett*., 2010, vol. 10, no. 7, pp. 2640-8.
75. Griep, M.H. et al., *Mol. Biol. Int*., 2012, vol. 2012, article ID 910707, 7 pages.