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«GREEN» SYNTHESIS OF NOBLE METAL NANOPARTICLES AND CdS SEMICONDUCTOR NANOCRYSTALS USING BIOLOGICAL MATERIALS

The basic principles of synthesis of metal nanoparticles and semiconductor nanocrystals as well as the prospects for their application have been discussed. The relevance of living systems and their components for the development of «green» technology for synthesizing nano-objects with unique properties and a wide range of applications has been analyzed. The biotechnological synthesis of silver, gold, and silver-gold bimetallic nanoparticles using plant extracts of Magnolia denudata, M. stellata, Camellia sinensis var. sinensis, C. sinensis var. assamica, Orthosiphon stamineus, and Hypericum perforatum has been described. The results of synthesis of cadmium sulfide fluorescent semiconductor nanocrystals using Escherichia coli bacteria, Pleurotus ostreatus basidiomycete and Linaria maroccana plant have been reported. Morphological and optical characteristics of the synthesized nanoparticles have been described.

Keywords: «green» synthesis of nanoparticles, biological synthesis of nanoparticles, phytochemical tanks, noble metal nanoparticles, bimetallic nanoparticles, semiconductor quantum dot nanoparticles, and fluorescent nanocrystals of cadmium sulfide.

Due to their unique properties, the precious metal nanoparticles and the semiconductor quantum dot nanoparticles (hereinafter referred to as «the quantum dots») have been increasingly used in the field of biological, biotechnological, and biomedical research. In particular, the metal nanoparticles are applied to the visualization of cells, subcellular structures, and processes in living organisms, the delivery of genes, drugs, and other targeted «cargo» to proper destinations, the hyperthermia treatment of tumors, etc. [1—3]. The quantum dots have high photostability and brightness and meet most of the criteria applying to fluorescent materials in biology. Therefore, they are used in anticancer therapy for imaging the intracellular structures, labeling the immunofluorescent proteins, detecting the toxins, etc. [4—6].

The traditional technologies for obtaining the nanoparticles of first generation are based on physical and chemical methods. They are energy intensive and involve the use of toxic substances. In addition, the effectiveness of nanomaterials in biology, biotechnology, and biomedicine essentially depends on the characteristics of nanoparticles, i.e. their size, shape, composition, and surface properties [7]. Given this, nowadays, it is extremely important to develop effective eco-friendly and cost-efficient methods for the synthesis of nanoparticles using biological systems [8]. In addition to lower burden on the environment and higher efficiency due to «greening» of nanoparticle synthesis, the use of biological systems and their components opens up additional oppor-

tunities for creating nanoparticles with required composition and properties. The biological methods for the nanoparticle synthesis are considered competitive with the conventional chemical and physical methods by speed, controllability, and conversion. The different approaches to the biological synthesis give the researchers a wide range of options for the selection of optimal parameters and the synthesis of given product for certain applications.

GENERAL DESCRIPTION OF EXISTING TECHNIQUES FOR SYNTHESIS OF METAL NANOPARTICLES AND SEMICONDUCTOR QUANTUM DOTS

The traditional methods of nanoparticle synthesis comprise the high-temperature condensation, the laser ablation, the vacuum evaporation of metals, the Svedberg electro-condensation, the radiolytic techniques, the reduction by polymeric surfactants, the reduction on soft and solid matrices, the use of polyoxometalates [9, 10], and others. The quantum dot nanoparticles are synthesized by molecular beam epitaxy, organometallic vapor phase epitaxy, e-beam lithography, growth in non-polar media, etc. [11, 12]. The application of these methods is associated with significant costs of energy and resources. It involves the use of toxic compounds, such as sodium borohydride, tetrakis (hydroxymethyl) phosphonium chloride, poly-N-vinylpyrrolidone, hydroxylamine, and others and the formation of a significant amount of toxic by-products [5, 8].

Unlike the above mentioned techniques, the biological methods are based on the use of biological metabolites, biological systems or their analogues for the synthesis of nanoparticles [13, 14]. If the process occurs inside a biological system utilizing its own metabolic pathways and resources, this is *biotechnological synthesis*. The biomimetic methods simulate certain processes that occur during the synthesis of nanoparticles *in vivo* involving certain biological compounds [1, 8, 14]. The biological methods of nanoparticle synthesis are expected to have greater efficiency and, consequently, to significantly reduce the cost of nanotechnology products [12—14]. In addition, the «biological» nanoparticles are assumed to have better biological compatibility, given the absence of adsorbed toxic substances. In general, the ecofriendly biological synthesis of nanoparticles and semiconductor quantum dot nanoparticles is based on the use of viruses [15], bacteria [16—20], actinomycetes [21, 22], fungi [23—25], and plants [26—31]. In addition, the research [32] describes the *in vitro* intracellular synthesis of gold nanoparticles by human cells of SiHa, SKNSH, HeLa, and HEK-293 lines.

MECHANISMS OF NANOPARTICLE BIOLOGICAL SYNTHESIS

The mechanisms of biological synthesis of nanoparticles have not been fully understood so far. Since the synthesis of nanoparticles is usually associated with chemical reduction of metal [33], the compounds of living cells able to act as reducing agents are studied. The biological synthesis of nanoparticles is believed to involve free amino acids, soluble proteins, enzymes, flavonoids, terpenoids, phenolic compounds, tannins, proanthocyanidins, carbohydrates, and vitamins [34, 35]. It has been found that during the extracellular synthesis of gold nanoparticles by *Fusarium oxysporum* Schlecht emend. Snyder & Hansen fungus, the metal reduces due to NADN-dependent reductase [36], while the synthesis of silver nanoparticles using *Enterobacteria sp.* involves nitrate reductase [37]. Proteins play a key role in the formation of silver nanoplates using an extract of unicellular green alga *Chlorella sp.* [38]. Protein amino groups «ensure» ion reduction and stabilization of silver nanoparticles in the synthesis using an extract of pepper *Capsicum annuum L.* [39]. A leading role in the synthesis of CdS nanocrystals by bacteria is assigned to enzymes [19, 20, 40]. In general, the type of compounds involved determines the properties (morphological characteristics, stability, reactivity) and place of localization of the final product, the nanoparticles, in terms of their synthesis (intra- or extra-

cellular) by living organisms. It is very relevant for developing commercial synthesis methods because of the fundamental importance of such factors as ease of extraction and further processing of nanoparticles. The rate of synthesis, structure, and morphology of nanoparticles synthesized by living organisms can be controlled by varying parameters such as pH, temperature, substrate concentration, and exposure time [33, 35, 38].

«GREEN» SYNTHESIS OF Au, Ag, AND BIMETALLIC AU/AG NANOPARTICLES

As mentioned above, the biological nanoparticle synthesis is based on the use of enzyme systems of biological objects and their organic compounds. Silver nitrate $AgNO_3$ and chloroauric acid $H[AuCl_4]$ or its sodium salt $NaAuCl_4$ are most commonly used as incoming inorganic substance for the «green» synthesis of silver and gold nanoparticles, respectively [13]. It should be noted that in the traditional chemical synthesis of nanoparticles, the most common reducing agents are citrate- and borohydride anions ($C_3H_5O(COO)_3^{3-}$ and $BH,^{4-}$ respectively) [1, 8]. The nanoparticles synthesized using the citrate anions are prone to aggregation and require stabilization by adding auxiliary agents. They are stable only in the initial (mother) liquor; they are unstable under *in vivo* conditions and actively interact with serum proteins. The nanoparticles reduced by borohydride anions are highly toxic to living organisms, in addition to the above disadvantages. The aggregation of unstable reactive nanoparticles is a limiting factor for the quality of final product [41], insofar as it decreases the area of specific surfaces and interfacial free energy, which impairs the reactivity of the particles [42]. The majority of methods of stabilization of nanoparticles synthesized by chemical and physical methods involves the use of dispersant molecules such as surfactants or polyelectrolytes. These substances not only change the chemical and physical parameters of the nanoparticle surface, but also generate a significant amount of waste as they constitute a big fraction [1]. In addition, many stabilizing agents are toxic to biological systems, which prevents the use of nanoparticles in many areas. The biological synthesis of nanoparticles makes it possible to avoid these restrictions.

Techniques for synthesizing nanoparticles of noble metals, silver (Ag) (Fig. 1), gold (Au) (Fig. 2), and Au/Ag bimetallic nanoparticles from silver nitrate ($AgNO_3$) and sodium tetrachloroaurate ($NaAuCl_4$)) using phytochemical containers have been developed [43—46]. The proposed group of methods is generally characterized by high efficiency and speed, is environmental friendly, feasible, and allows the researchers to obtain highly stable nanoparticles of controlled morphology in macro-quantities for their use in biological and biomedical applications. In addition, unlike the traditional methods of synthesis, the biotechnological synthesis prevents the reducing and stabilizing agents from absorption on the nanoparticle surface and, consequently, eliminates the toxicity of final nano-products. In this approach, the nanoparticles are stabilized in the course of synthesis due to the presence of plant metabolites having a specific activity in the reaction mixture. Thus, this method realizes the *one pot* approach aimed at simplifying, cheapening, and raising efficiency of large-scale synthesis of compounds, substances, and materials.

For obtaining Au, Ag, and Au/Ag nanoparticles, silver nitrate ($AgNO_3$) and sodium tetrachloroaurate ($NaAuCl_4$) are added to aqueous extracts of plant biomass. Aqueous extracts from leaves of *Magnolia denudata* Desr. and *M. stellata* (Siebold & Zucc.) Maxim., *Camellia sinensis* var. sinensis (L.) Kuntze and *C. sinensis* var. *assamica* (JW Mast.) Kitam., *Orthosiphon stamineus* Benth., and *Hypericum perforatum* L are used as phytochemical container. In general, all these plants are characterized by the ability to accumulate significant quantities of metabolites that act as reducing agents, including amino acids, proteins, flavonoids, phenolic compounds, tannins, carbohydrates, etc. [30, 33, 34]. This ability is of paramount importance for the successful synthesis and stabilization of nanoparticles.

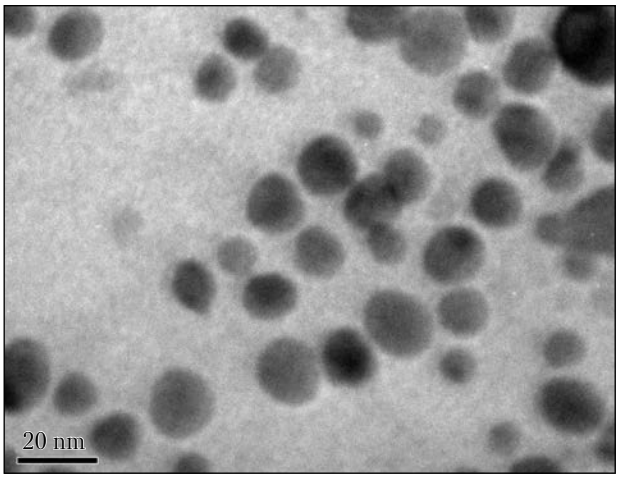

Fig. 1. Electron microscope image of silver nanoparticles synthesized using phyto extracts. Calibration mark: 20 nm

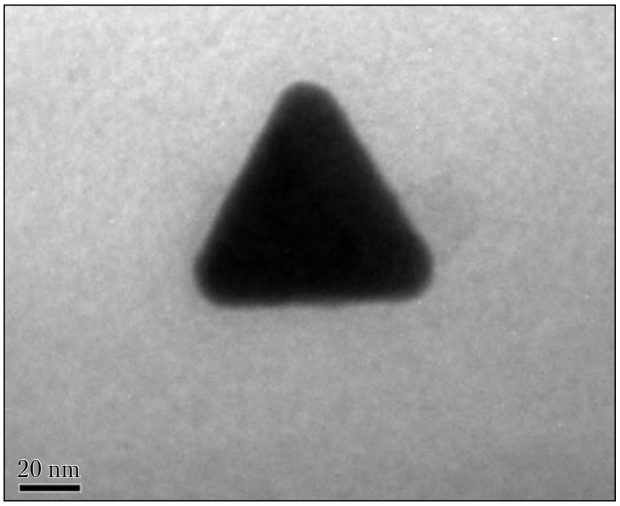

Fig. 2. Electron microscope image of gold nanoparticles synthesized using phyto extracts and soft matrix. Calibration mark: 20 nm

In addition, having compared the research results, the effectiveness of using different phytoextracts for the synthesis of nanoparticles is established to depend on the composition of extracts of various plants, as well as on specific processes of reduction of silver and gold ions. Thus, the use of magnolia extracts is effective for obtaining silver, gold, and Au/Ag bimetallic nanoparticles. The extracts of Hypericum and Orthosiphon are effective only for getting silver nanoparticles, while the green tea extracts have demonstrated their effectiveness for synthesizing gold nanoparticles. During the formation of metal nanoparticles, the reaction mixture changes its color, as a result of surface plasmonic resonance in formed nanoscale structures. The colloidal solutions of gold nanoparticles are tinged with red, while those of silver nanoparticles are tinted with tan, and those of bimetallic nanoparticles are of middle tints. The direct irradiation of reaction mixture with sunlight has been established to speed up the formation of silver nanoparticles and not to affect that of gold nanoparticles. The rate of nanoparticle formation has been found to depend directly on the temperature of synthesis, whereas their size has showed an inverse temperature dependence. This is obviously due to the influence of temperature on the correlation of nucleation intensity and nanoparticle growth. Maximum absorption of synthesized silver nanoparticles is located near a wavelength of 450 nm; that of gold particles is reported for a wavelength of near 540 nm. The size of silver and gold nanoparticles obtained at a temperature of 90—95 °C ranges 25—30 nm and 3—10 nm, respectively. Due to varying temperature, the researchers have obtained nanoparticles of desired size. The resulting silver and gold nanoparticles are stable in colloidal aqueous solution for several months and show high antibacterial effect [45, 46].

Having analyzed the samples using the transmission electron microscopy (TEM) method, the nanoparticles of noble metals synthesized from phytoextracts are established to have mostly spherical shape (Fig. 1). The nanoparticles of different morphology has been demonstrated to be synthesized by adding cationic surfactant cetyl trimethylammonium bromide (CTAB) as soft matrix to the reaction mixture (Fig. 2). The technique of seed-induced growth in the reaction medium containing CTAB clusters has been applied to obtain poly-metallic (bimetallic) nanoparticles. The synthesis of bimetallic particles was carried out in two phases because of different rates of reduction of silver and gold ions, which caused the agglom-

eration of products and the formation of uneven coating of silver quasi-spherical nanoparticles and impurities. At the first phase, the gold nanorods were synthesized by seed-induced reduction of sodium tetrachloroaurate in the presence of CTAB. Later, the gold nanorods were separated and used as core for the synthesis of bimetallic nanorods by indirect reduction of silver (caused by phytoextract components) on the surface of gold rods. The TEM study has showed the formation of spherical and triangular nanoparticles having a size of about 20 nm and of nanorods having a length of about 100 nm (Fig. 3). Insofar as the formation of metal nanoparticles using phyto containers is based on the chemical reduction of metal, it is clear that this process involves reducing agents. In a more wide context, these agents can be identified with herbal antioxidants. The results of Fourier-transforming infrared spectroscopy and Raman spectroscopy of mother solutions and colloids of synthesized nanoparticles give reason to assume an important role in the synthesis of such plant metabolites as flavonoids, amino acids, sugars, proteins, and phenolic compounds.

The proposed methods for the synthesis of noble metal nanoparticles make it possible to obtain nanoparticles of controllable size and morphology in an environmental friendly and resource-saving way. In addition, the technology is easy scalable and can be implemented in various fields.

SYNTHESIS OF CDS SEMICONDUCTOR QUANTUM DOTS

The fluorescent semiconductor nanocrystals known as quantum dots are composed of 10—50 atoms. Their diameter is about 2—10 nm [5]. They consist of a semiconductor core surrounded by a shell of elements of II—VI or III—V groups of the periodic system. As mentioned above, the nanocrystals are characterized by unique optical and optoelectronic properties suitable for a wide range of applications. In particular, thanks to a wide range of absorption spectra the quantum dots emit within a narrow range of wavelengths and have a high photostability and brightness. The nanocrystal fluorescence color is controlled during the synthesis, because it depends on the chemical composition, surface properties, and size. In general, the fluorescence color changes from red to blue part of the spectrum the size of quantum dots decreases, with the intensity of radiation increasing [4]. The described dependence of optical properties of nanocrystals on their size is determined by the effect of quantum spatial confinement.

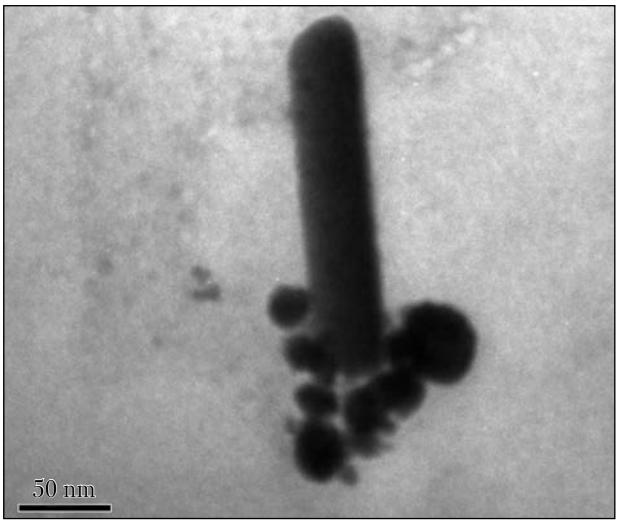

Fig. 3. Electron microscope image of nanorods obtained in the course of synthesis of bimetallic Au/Ag particles using phyto extracts and soft matrix. Calibration mark: 50 nm

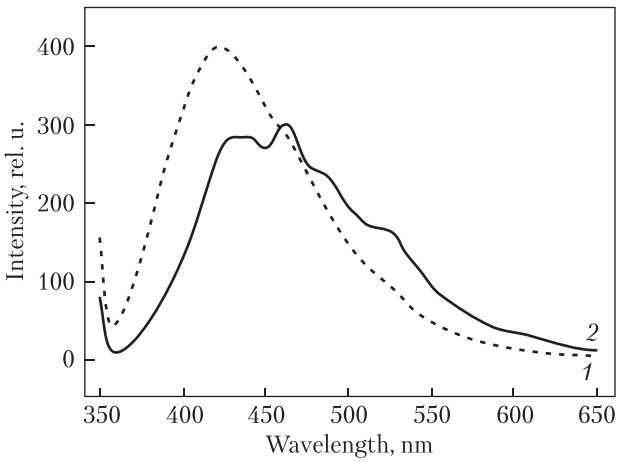

Fig. 4. Photoluminescence spectrum of pure culture of *P. ostreatus* fungus (*1*); photoluminescence spectrum of quantum dots obtained using *P. ostreatus* fungus culture (*2*)

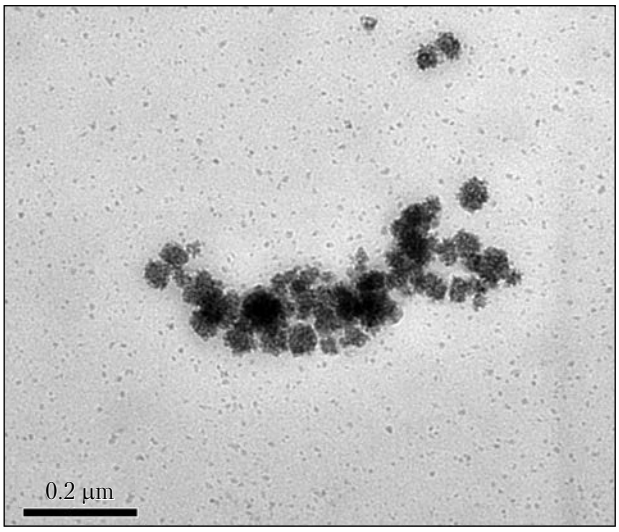

Fig. 5. Electron microscope image of CdS quantum dot conglomerates obtained using *P. ostreatus* fungus. Calibration mark: 0.2 μm

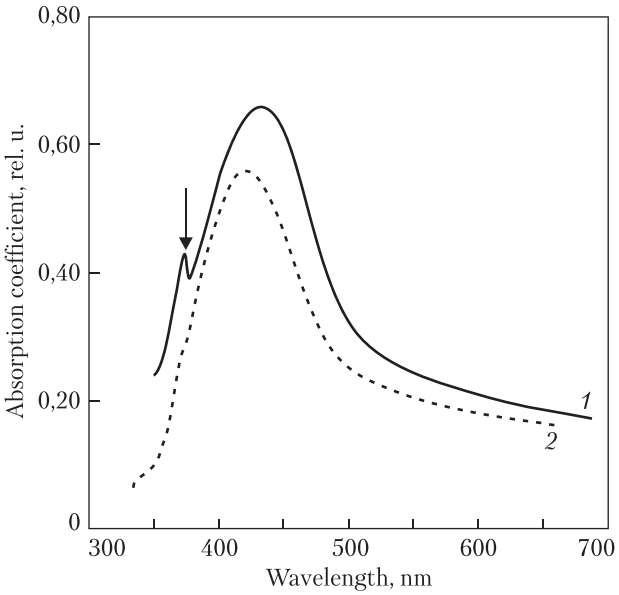

Fig. 6. Absorption spectrum of CdS quantum dots obtained using *E. coli*: (*1*) immediately after the synthesis; (*2*) in 10 days

Today, the CdS nanocrystals are of considerable interest because of their possible use in biology and biomedicine as fluorescent labels for the detection of subcellular structures and individual molecules of compounds. The traditional methods of their synthesis (like those of the synthesis of precious metal nanoparticles) are environmentally hazardous, high-cost, and very sophisticated that results in high cost and high toxicity of the final product. The authors hereof have developed a method for biotechnological synthesis of cadmium sulfide nanoparticles using the biosystems of basidiomycete *Pleurotus ostreatus* (Jacq.) P. Kumm. (Figs. 4, 5) [47], bacteria *Escherichia coli* (Migula) Castellani et Chalmers (Fig. 6, 7) [48], and plant *Linaria maroccana* L. (Fig. 8, 9) [49].

The fungal systems are effective for the synthesis of CdS nanocrystals inasmuch as they contain sulfate reductase enzymes that reduce the sulfate groups of metal salt directly into the culture medium. The result is the formation of extracellular CdS nanoparticles. In addition, the fungi have high performance of the synthesis and secretion of enzymes, as well as protein and carbohydrate compounds. Given this, the technique for the industrial synthesis of quantum dot nanoparticles using fungi is very promising in terms of high output of nanoparticles [1, 3, 21, 22]. The authors are the first who have demonstrated the successful biological synthesis of CdS using *Pleurotus ostreatus* [47]. The optical absorption spectroscopy is known to be an effective method for both establishing the existence of nanoparticles in the studied samples and estimating the size of these particles [50]. In particular, the large crystallites (>10 nm) are characterized by the absorption close to that of single crystals, while the nanoparticles smaller than 10 nm are characterized by a «blue» shift that corresponds to a widened band gap [51]. The study of absorption spectra has showed that the nanoparticles synthesized using fungi have a broad dome-shaped absorption spectrum with a maximum at λ_{max} ~ 453 nm (for the single crystals of this size the peak is ~515 nm), which is typical for the CdS nanocrystals given the «blue» shift. Fig. 4 shows a photoluminescence spectrum obtained by excitation of a sample containing CdS quantum dots with a radiation (wavelength λ = 340 nm) (curve 2) as compared with a photoluminescence spectrum of so-

lution of pure culture medium of *P. ostreatus* (curve 1). The luminescence of culture medium is characterized by a broad domed band, while that of synthesized samples has a much more complex shape. In particular, there are several distinct maxima at wavelengths of 431, 462, 486, and 524 nm. These peaks correspond to excitonic bands of nanoparticles of different sizes [47]. Using the TEM technique, the synthesized CdS quantum dots have been established to form spherical conglomerates having a diameter of 40—70 nm (Fig. 5). Within these clusters, the CdS quantum dots have a spherical shape, uniform morphology, and a diameter of 5—8 nm.

The advantage of using the microorganisms to develop efficient methods for the synthesis of quantum dots as compared with other biological objects is their ability to function in an environment under stressful conditions, particularly, in the presence of high concentration of metals, as well as under sudden changes in temperature, pH, and pressure [48]. Among the microorganisms, the *E. coli* bacterium is potentially one of the most effective objects for the biosynthesis of semiconductor nanocrystals given a relative simplicity, ease and rapidity of commercial cultivation, and the ability of *E. coli* to secrete into the culture medium a set of metabolites involved in the synthesis of quantum dots. The authors have synthesized CdS quantum dots using *E. coli* bacterial culture [48]. Based on the study of the absorption and luminescence spectra, the resulting nano-product has been showed to have high stability over time; new synthesized CdS semiconductor nanoparticles have been established to have a size ranging 2.5—2.6 nm. Within 10 days, these nanocrystals form clusters of 4—8 nm; this dense fraction of nanoparticles is stored in the sample for 3 months. In the short-range part of the spectrum of newly synthesized nanocrystals, there is a narrow band with a maximum at a wavelength of 368 nm (Fig. 6). According to the literature data, the nanoparticles smaller than 3 nm the excitonic absorption manifests itself as intense sharp peak [52]. The absorption spectrum of nanoparticles in

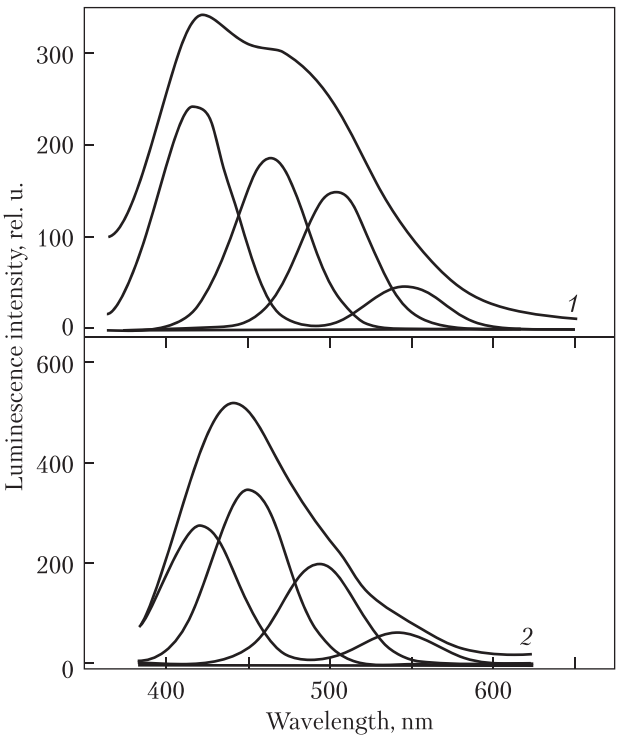

Fig. 7. Photoluminescence spectrum of CdS quantum dots obtained using *E. coli*: (*1*) immediately after the synthesis; (*2*) in 10 days

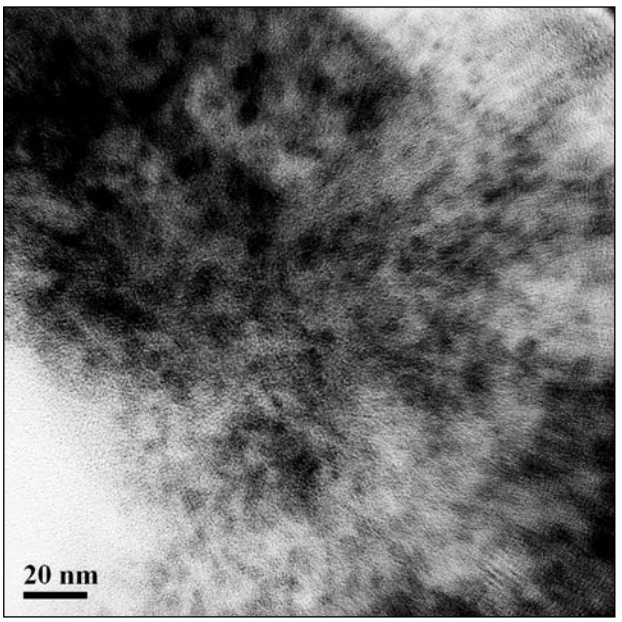

Fig. 8. Electron microscope image of CdS quantum dot conglomerates obtained using *E. coli*. Calibration mark: 20 nm

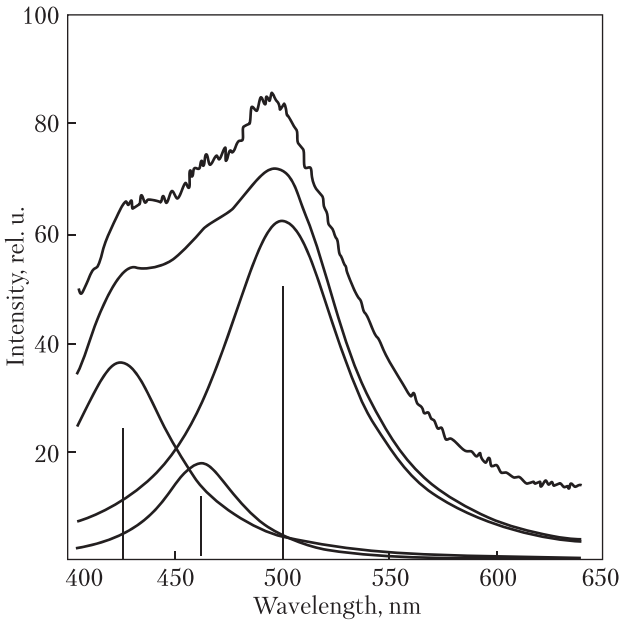

Fig. 9. Photoluminescence spectrum of CdS quantum dots obtained using hairy root culture extracts of *L. maroccana*

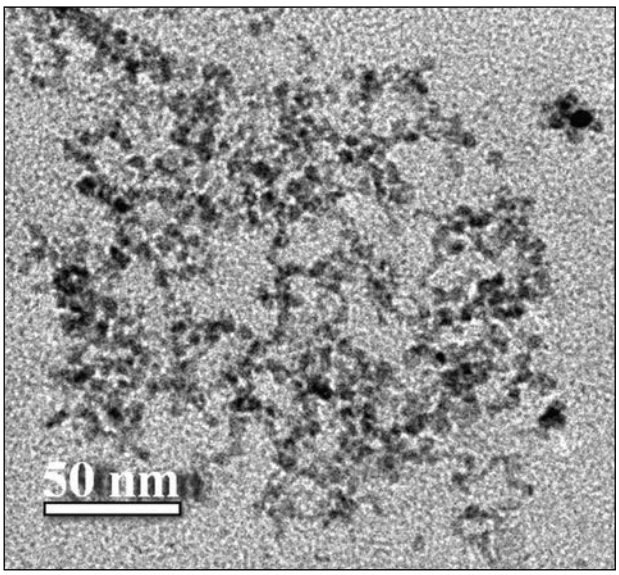

Fig. 10. Electron microscope image of CdS quantum dot conglomerates obtained using hairy root culture extracts of *L. maroccana*. Calibration mark: 50 nm

10 days after the synthesis is shaped as a broad band with a maximum at 420—430 nm, which corresponds the absorption by objects having a size ranging 4—8 nm. Fig. 7 shows photoluminescence spectra of laser-excited objects at a wavelength $\lambda = 345$ nm, which correspond to the newly synthesized samples (solid curve 1) and to the 10-day aged samples (solid curve 2). The spectral profile was divided into components described by the Gaussians of equal width. Four Gaussians appeared to be enough for the correct division of spectra. Each Gaussian corresponds to luminescence of nanoparticles having a certain diameter. As one can see in Fig. 7, the luminescence spectrum of newly synthesized samples is shaped as a broad band with peaks at wavelengths of 422 and 470 nm, with the Gaussian that has a maximum at 417 nm being the most intensive among the four ones (it corresponds to the fraction of the smallest nanoparticles). In 10 days after the synthesis, the spectrum is shaped as a more symmetrical narrow band with a maximum at a wavelength of 443 nm. In this case, the intensity of spectral components is redistributed in a way that the Gaussian with a maximum at 459 nm is the most intense one. The last fact means a gradual aggregation of nanoparticles, as a result of which the fraction of larger nanoparticles grows. It should be noted that due to the partial aggregation, the formed nanostructures are stable for 3 months after synthesis, as their photoluminescence spectrum remains unchanged. Using the X-ray analysis, the authors have obtained electron diffraction patterns of CdS samples deposited on a copper-carbon grid. The diffraction maxima correspond to interplanar distances of 0.341, 0.209, and 0.1876 nm. These interplanar distances correspond to CdS crystals (wurtzite modification). In addition, using the TEM technique, the synthesized CdS quantum dots have been established to have a nearly spherical shape and a diameter within the range of 4—8 nm and to be free of surface flaws and defects (Fig. 8). According to [53], the *E. coli* bacteria have endogenous capacity for synthesis of CdS nanoparticles in the presence of appropriate inorganic salts. The authors thereof point out that the ability to form CdS nanocrystals strongly depends on the strain

of bacteria and phase of its development in culture. This research has confirmed that *E. coli* cell culture is an effective biological container for synthesizing cadmium sulfide quantum dots. For the optimal effect, the bacterial culture should be used in the stationary phase of its development.

As of today, the biosynthesis of semiconductor nanoparticles using plants has not been completely studied. However, the use of plant extracts for the creation of nano-objects has been economically justified and environment friendly [31]. The authors hereof have presented a method of «green» synthesis of CdS nanocrystals using extracts of transgenic culture *Linaria maroccana* L. [49]. It should be noted that the biomass of the plant is able to accumulate a significant amount of alkaloid D, L-peganine, flavonoid glycosides, ascorbic acid, pectin compounds, etc. Presumably, these compounds may be involved in the formation of stable CdS semiconductor nanoparticles in cells. The size of nanoparticles synthesized from *L. maroccana* ranges 2—8.5 nm. The spectrum of visible luminescence has three maxima at wavelengths of 425, 462, and 500 nm (Fig. 9). The TEM analysis has showed that the obtained CdS nanoparticles are of elliptical or nearly spherical shape and have no significant surface flaws (Fig. 10).

CONCLUSIONS

The synthesized CdS nanocrystals have absorption and luminescence spectra typical for quantum dots, elliptical or nearly spherical shape and size ranging from 1.5 to 9 nm. They keep stable for a long time. In the future, it is possible to control the size of CdS nanoparticles, which is the critical parameter for their application, by varying the synthesis conditions. The CdS nanoparticles synthesized by the described «green» technique are promising in terms of their use in biological field, particularly, as a new class of fluorophores.

In general, the nanoparticles synthesized using biological materials have several distinct advantages: controlled size, higher *in vivo* stability, nontoxicity, safety, biological compatibility, and compliance with the principles of «green» chemistry. The authors hereof have developed an efficient, environmentally friendly «green» technology for synthesizing nanoparticles of noble metals and quantum dots using biological systems. The use of biological systems and their components has been showed not only to reduce burden on the environment, but also to open up the opportunity for creating high-quality nanoparticles with desired morphological parameters for various applications in biology and biomedicine.

REFERENCES

1. Mohanpuria, P., Rana, N., and Yadav, S.: Biosynthesis of Nanoparticles: Technological Concepts and Future Applications. *J. Nanopart. Res.*, 10, 507—517 (2008).
2. Tam, J.M., Tam, J.O., Murthy, A. et al.: Controlled Assembly of Biodegradable Plasmonic Nanoclusters for Near-Infrared Imaging and Therapeutic Applications. *ACS Nano*, 4, 2178—2184 (2010).
3. Burlaka, O.M., Pirko, Ya.V., Yemets, A.I., and Blume, Ya. B.: «Green» Synthesis of Metal Nanoparticles: Capacity of Biological Systems and Prospects for Development. *Nanostructure Material Science*, 4, 89—103 (2012) (in Ukrainian).
4. Sarwat, B.R., Ghaderi, S., Keshtgar, M., and Seifalian, A.M.: Semiconductor Quantum Dots as Fluorescent Probes for In Vitro and In Vivo Bio-Molecular and Cellular Imaging. *Nano Rev.*, 1, 1—15 (2010).
5. Singh, S.H., Bozhilov, K., Mulchandani, A. et al.: Biologically Programmed Synthesis of Core-Shell CdSe/ZnS Nanocrystals. *Chem. Commun.*, 46, 1473—1475 (2010).
6. Michalet, X., Pinaud, F.F., and Bentolila, L.A.: Quantum Dots for Live Cells, *In Vivo* Imaging, and Diagnostics. *Science*, 307, 5709, 538—544 (2005).
7. Dahl, J.A., Maddux, B.L.S., and Hutchison, J.E.: Toward Greener Nanosynthesis. *Chem. Rev.*, 107, 2228—2269 (2007).
8. Iravani, S.: Green Synthesis of Metal Nanoparticles Using Plants. *Green Chem.*, 13, 2638—2650 (2011).
9. Krutiakov, Yu.A., Kudrinski, A.A., Olenin, A.Yu., and Lisichkin, G.V.: Synthesis and Properties of Silver Nanoparticles: Achievement and Prospects. *Uspekhi Khimii*, 77, 3, 242—269 (2008) (in Russian).
10. Darroudi, M., Ahmad, M.B., Zamiri, R. et al.: Time-Dependent Effect in Green Synthesis of Silver Nanoparticles. *Int. J. Nanomedicine*, 6, 677—681 (2011).
11. Nirmal, M., Dabbousi, B.O., Bawendi, M.G., Brus, L.E. et al.: Fluorescence Intermittency in Single Cadmium Selenide Nanocrystals. *Nature*, 383, 802—804 (1996).
12. Gaponik, N., Talapin, D.V., Rogach, A.L. et al.: Thiol-Capping of CdTe Nanocrystals: an Alternative to Orga-

nometallic Synthetic Routes. *J. Phys. Chem.*, 106, 7177—7185 (2002).
13. Shankar, S.S., Rai, A., Ahmad, A., and Sastry, M.: Rapid Synthesis of Au, Ag, and Bimetallic Au Core—Ag Shell Manoparticles Using Neem (Azadirachta indica) Leaf Broth. *J. Coll. Interface Sci.*, 275, 496—502 (2004).
14. Song, J.Y. and Kim, B.S.: Rapid Biological Synthesis of Silver Nanoparticles Using Plant Leaf Extracts. *Bioproc. Biosyst. Eng.*, 32, 79—84 (2009).
15. Lim, J.-S., Kim, S.-M., Lee, S.-Y. et al.: Formation of Au/Pd Alloy Nanoparticles on TMV. *J. Nanomater.*, 6, 620505—620511 (2010).
16. Nair, B. and Pradeep, T.: Coalescence of Nanoclusters and Formation of Submicron Crystallites Assisted by Lactobacillus Strains. *Cryst. Growth. Des.*, 2, 293—298 (2002).
17. Kannan, N. and Subbalaxmi, S.: Green Synthesis of Silver Nanoparticles Using Bacillus Subtillus IA751 and Its Antimicrobial Activity. *Res. J. Nanosci. Nanotechnol.*, 1, 2, 94—97 (2011).
18. Manonmani, V. and Vimala, J.: Biosynthesis of Ag Nanoparticles for the Detection of Pathogenic Bacteria in Food. *2011 Int. Conf. Innovat., Management Service IPEDR.*, 14, 311 (2011).
19. Mousavi, R.A, Akhavan, S.A., and Fazeli, M.R.: Biosynthesis, Purification and Characterization of Cadmium Sulfide Nanoparticles Using Enterobacteriaceae and Their Application. *Nanomater. Appl. Proper.*, 1, 1, 1—5 (2012).
20. Dameron, C.T., Reese, R.N., and Mehra, R.K.: Biosynthesis of Cadmium Sulphide Quantum Semiconductor Crystallites. *Nature*, 338, 13, 596—597 (1989).
21. Ahmad, A., Senapati, S., Khan, M.I. et al.: Intracellular Synthesis of Gold Nanoparticles by a Novel Alkalotolerant Actinomycete, Rhodococcus sp. *Nanotechnol.*, 14, 824 — 828 (2003).
22. Ahmad, A., Senapati, S., Khan, M.I. et al.: Extracellular Biosynthesis of Monodisperse Gold Nanoparticles by a Novel Extremophilic Actinomycete, Thermomonospora sp. *Langmuir,* 19, 3550—3553 (2003).
23. Bansal, V., Poddar, P., Ahmad, A., and Sastry, M.: Room-Temperature Biosynthesis of Ferroelectric Barium Titanate Nanoparticles. *J. Am. Chem. Soc.*, 128, 11958—11963 (2006).
24. Vigneshwaran, N., Ashtaputre, N.M., Varadarajan, P.V. et al.: Biological Synthesis of Silver Nanoparticles Using the Fungus Aspergillus flavus. *Mat. Lett.*, 61, 1413—1418 (2007).
25. Kumar, S.A., Ayoobul, A.A., Absar, A., and Khan, M.I.: Extracellular Biosynthesis of CdSe Quantum Dots by the Fungus, Fusarium oxysporum. *J. Biomed. Nanotechnol.*, 3, 190—194 (2007).
26. Arjunan, K., Murugan, K., Rejeeth, C. et al.: Green Synthesis of Silver Nanoparticles for the control of Mosquito Vectors of Malaria, Filariasis, and Dengue. *Vector Borne Zoonotic Dis.*, 12, 3, 262—269 (2012).
27. Jayaseelan, C., Rahuman, A.A., Rajakumar, G. et al.: Synthesis of Pediculocidal and Larvicidal Silver Nanoparticles by Leaf Extract from Heartleaf Moonseed Plant, Tinospora cordifolia Miers. *Parasitol. Res.*, 109, 185—194 (2011).
28. Guidelli, E.J., Ramos, A.P., Zaniquelli, M.E.D., and Baffa, O.: Green Synthesis of Colloidal Silver Nanoparticles Using Natural Rubber Latex Extracted from Hevea brasiliensis. *Spectrochimica Acta A*, 82, 140—145 (2011).
29. Kaviya, S., Santhanalakshmi, J., and Viswanathan, B.: Green Synthesis of Silver Nanoparticles Using Polyalthia longifolia Leaf Extract along with D-sorbitol: Study of Antibacterial Activity. *J. Nanotechnol.* (2011); http://www.hindawi.com/journals/jnt/2011/152970.
30. Mallikarjuna, K., Narasimha, G., Dillip, G.R. et al.: Green Synthesis of Silver Nanoparticles Using Ocimum Leaf Extract and Characterization. *Digest J. Nanomater. Biostruct.*, 6, 1, 181—186 (2011).
31. Marchiol, L.: Synthesis of Metal Nanoparticles in Living Plants. *Italian J. Agron.*, 7, 3, 274—282 (2012).
32. Anshup, A., Venkataraman, J.S., Subramaniam, C. et al.: Growth of Gold Nanoparticles in Human Cells. *Langmuir*, 21, 11562—11567 (2005).
33. Satyavani, K., Ramanathan, T., and Gurudeeban, S.: Plant Mediated Synthesis of Biomedical Silver Nanoparticles by Using Leaf Extract of Citrullus colocynthis. *Res. J. Nanosci. Nanotechnol.*, 1, 2, 95—101 (2011).
34. Virkutyte, J. and Varma, R.S.: Green Synthesis of Metal Nanoparticles: Biodegradable Polymers and Enzymes in Stabilization and Surface Functionalization. *Chem. Sci.*, 2, 837—846 (2011).
35. Shukla, R., Nune, S.K., Chanda, N. et al.: Soybeans as a Phytochemical Reservoir for the Production and Stabilization of Biocompatible Gold Nanoparticles. *Small.*, 4, 9, 1425—1436 (2008).
36. Mukherjee, P., Senapati, S., Mandal, D. et al.: Extracellular Synthesis of Gold Nanoparticles by the Fungus Fusarium oxysporum. *Chem. Bio. Chem.*, 3, 461—463 (2002).
37. Shahverdi, A., Minaeian, S., Shahverdi, H.R. et al.: Rapid Synthesis of Silver Nanoparticles Using Culture Supernatants of Enterobacteria: a Novel Biological Approach. *Proc. Biochem.*, 42, 919—923 (2007).
38. Xie, J., Lee, J.Y., Wang, D.I.C., and Ting, Y.P.: Silver Nanoplates: from Biological to Biomimetic Synthesis. *ACS Nano*, 1, 429—439 (2007).
39. Li, S., Shen, Y., Xie, A. et al.: Green Synthesis of Silver Nanoparticles Using Capsicum annuum L. extract. *Green Chem.*, 9, 852—858 (2007).
40. Li, X., Xu, H., Chen, Zh-Sh., and Chen, G.: Biosynthesis of Nanoparticles by Microorganisms and Their Applications. *J. Nanomater.*, 1—16 (2011).
41. Pomogailo, A.D., and Kestelman, V.N. (2005). Metallopolymer Nanocomposites. Springer: Berlin, Heidelberg, New York.

42. He, F., Zhao, D., Liu, J., and Roberts, C.B.: Stabilization of Fe-Pd Bimetallic Nanoparticles with Sodium Carboxymethyl Cellulose for Enhanced Degradation of TCE in Water. *Ind. Eng. Chem. Res.*, 46, 29—34 (2007).
43. Blume, Ya.B., Pirko, Ya.V., Danilenko, I.A. et al.: Technique for Obtaining Silver and Gold Nanoparticles. Patent of Ukraine for Utility Model no. 86778 of 10.01.2014 (in Ukrainian).
44. Pirko, Ya., Danylenko, I., Kolomys, O. et al.: Phytochemical Mediated Synthesis of Silver and Gold Nanoparticles. *Curr. Pharm. Biotechnol.*, 13, 15, 85 (2012).
45. Pirko, Ya., Danylenko, I., Kolomys, O. et al.: Synthesis of Silver Nanoparticles Using Phytoextracts from Higher Plants. *Chemistry-2011: 10th Int. Conf. Lithuanian Chemists*, 135 (2011).
46. Danilenko, I.A., Botvinko, A.V., Pirko, Ya.V. et al.: Synthesis and Antibacterial Properties of Silver Nanoparticles Synthesized Using Phytoextracts. *Nanosize Systems: Structure, Properties, and Technologies*, 472 (2013) (in Ukrainian).
47. Borova, M.M., Naumenko, A.P., Pirko, Ya.V., Krupodiorova, T.A., Yemets, A.I., and Blume, Ya.B.: Obtaining CdS Quantum Dots Using Pleurotus ostreatus. *Reports of the NAS of Ukraine*, 2, 153—159 (2014) (in Ukrainian).
48. Borova, M.M., Naumenko, A.P., Yemets, A.I., and Blume, Ya.B.: Stability of CdS Quantum Dots Synthesized Using Escherichia coli Bacterium. *Reports of the NAS of Ukraine,* 7, 145—151 (2014) (in Ukrainian).
49. Borovaya, M.N., Naumenko, A.P., Matvieieva, N.A. et al.: Biosynthesis of Luminescent CdS Quantum Dots Using Plant Hairy Root Culture. *Nanoscale Res. Lett.*, 9 (2014).
50. Martínez-Castañón, G.A, Loyola-Rodríguez, J.P, and Reyes-Macías, J.F.: Synthesis and Optical Properties of Functionalized CdS Nanoparticles with Different Sizes. *Superficies y vacío*, 23, 4, 1—4 (2010).
51. Asaula, V.N., Mirnaia, T.A., and Yaremchuk, G.G.: Nanostructured Liquid Crystal Systems of Metal Alcanoates with CdS Nanoparticles. *Nanosystems, Nanomaterials, and Nanotechnologies*, 10, 1, 193—201 (2012) (in Russian).
52. Rossetti, R, Ellison, J.L, Gibson, J.M, and Brus, L.E.: Size Effects in the Excited Electronic States of Small Colloidal CdS Crystallites. *J. Chem. Phys.,* 80, 9, 4464—4469 (1984).
53. Sweeney, R.Y., Mao, C., and Gao, X.: Bacterial Biosynthesis of Cadmium Sulfide Nanocrystals. *Chem. Biol.*, 11, 11, 1553—1559 (2004).

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«ЗЕЛЕНИЙ» СИНТЕЗ НАНОЧАСТИНОК БЛАГОРОДНИХ МЕТАЛІВ ТА НАПІВПРОВІДНИКОВИХ НАНОКРИСТАЛІВ CdS ЗА ДОПОМОГОЮ БІОЛОГІЧНОЇ СИРОВИНИ

Розглянуто основоположні принципи синтезу наночастинок металів і напівпровідникових нанокристалів та перспективи його застосування. Проаналізовано актуальність використання живих систем і їх компонентів для розробки технологій «зеленого» синтезу нанооб'єктів із винятковими властивостями та широким спектром застосувань. Описано біотехнологічний синтез наночастинок срібла, золота та біметалічних срібно-золотих наночастинок з використанням екстрактів рослин *Magnolia denudata*, *M. stellata*, *Camellia sinensis* var. *sinensis*, *C. sinensis* var. *assamica*, *Orthosiphon stamineus* та *Hypericum perforatum*. Наведено результати отримання флуоресцентних напівпровідникових нанокристалів сульфіду кадмію за допомогою бактерії *Escherichia coli*, базидіального гриба *Pleurotus ostreatus* та рослини *Linaria maroccana*. Представлено морфологічні та оптичні характеристики синтезованих наночастинок.

Ключові слова: «зелений» синтез наночастинок, біологічний синтез наночастинок, фітохімічні ємкості, наночастинки благородних металів, біметалічні наночастинки, напівпровідникові квантові точкові наночастинки, флуоресцентні нанокристали сульфіду кадмію.

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«ЗЕЛЕНЫЙ» СИНТЕЗ НАНОЧАСТИЦ БЛАГОРОДНЫХ МЕТАЛЛОВ И ПОЛУПРОВОДНИКОВЫХ НАНОКРИСТАЛЛОВ CdS С ПОМОЩЬЮ БИОЛОГИЧЕСКОГО СЫРЬЯ

Рассмотрены основоположные принципы синтеза наночастиц металлов и полупроводниковых нанокристалов, а также перспективы его применения. Проанализирована актуальность перспективы использования живых систем и их компонентов для разработки «зеленых» технологий синтеза нанообъектов с исключительными свойствами и широким спектром применений. Описан биотехнологический синтез наночастиц серебра, золота и биметаллических серебряно-золотых наночастиц с использованием экстрактов растений *Magnolia denudata, M. stellata, Camellia sinensis* var. *sinensis, C. sinensis* var. *assamica, Orthosiphon stamineus* и *Hypericum perforatum*. Приведены результаты получения флуоресцентных полупроводниковых нанокристаллов сульфида кадмия с помощью бактерии *Escherichia coli*, базидиального гриба *Pleurotus ostreatus* и растения *Linaria maroccana*. Представлены морфологические и оптические характеристики синтезированных наночастиц.

Ключевые слова: «зеленый» синтез наночастиц, биологический синтез наночастиц, фитохимические емкости, наночастицы благородных металлов, биметаллические наночастицы, полупроводниковые квантовые точечные наночастицы, флуоресцентные нанокристаллы сульфида кадмия.

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