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Reviews

Promising avenues of research in nanoscience: chemistry of semiconductor nanoparticles*

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The state-of-the-art in the field of research on semiconductor nanoparticles is analyzed; cadmium chalcogenide nanoparticles are considered in most detail. Emphasis is placed on the methods of synthesis and on control of the size, composition, and structure of semiconductor nanoparticles — "quantum dots". The state of the surface plays a significant role in determining the properties of nanoparticles. Organized nanostructures comprised of quantum dots are considered. The properties of semiconductor nanoparticles are described. Prospects for applications of semiconductor nanomaterials are discussed.

Key words: nanoparticles, quantum dots, semiconductor materials, nanoscience, nanotechnology.

1. Introduction

Nanoscience is a field of knowledge of the properties of matter in the nanostate. The subject of nanoscience is investigation of fundamental mechanisms of structure formation, structural organization and transformation at a nanolevel in organic, inorganic, hybrid organo-inorganic, and biological systems and involves complex interdisciplinary investigations of the physical and chemical properties of nanoscale objects.

Nanoscience serves as a basis for nanotechnology. The main goal of the latter is to develop economically and environmentally efficient methods for the design of novel nanostructured materials and highly disperse systems, preparation of films and coatings, fabrication of functional nanostructures and elements of nanoelectronic devices that are promising for applications in various fields from the information and telecommunication systems, optoelectronics, and catalysis to medicine and bioengineering.

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Tremendous progress of nanoscience and nanotechnology involves researchers working in different fields. The main goal of this review is to analyze the advances in one of the key avenues of nanoscience — chemistry of semiconductor nanoparticles — and to reveal trends and promising avenues of future development.

Semiconductor materials are basic to modern electronic devices. A characteristic trend of progress in electronics is continuous miniaturization of functional elements and corresponding increase in the degree of integration of integrated circuits and other devices.

Miniaturization of functional elements of integrated circuits down to the nanolevel using conventional technologies faces two serious problems. First, electronic, optical, magnetic and other properties of nanomaterials can be significantly different from the properties of corresponding bulk phases. The nanolevel is also characterized by manifestation of novel physical effects, *e.g.*, electron tunneling, size quantization of energy levels, *etc*. Second, traditionally used methods of fabrication of functional elements for planar technologies, which involve a number of lithographic processes, approach the physical limit of the resolution of lithographic systems and cause economic problems due to exponential increase in the cost of production of more and more miniature devices.

It is believed[1] that the advancement of technologies to the nanolevel and the development of real nanotechnologies requires economically efficient, simple (as simple as possible), and environmentally friendly approaches. In our opinion, chemical synthesis, functionalization, ordered spatial organization of nanoparticles, and design of nanomaterials and devices based on them meet these common requirements. Methods of synthesis as well as the structure and properties of nanoparticles have been considered in a monograph[2] and in a collection of works.[3]

Researchers first interested in semiconductor nanocrystals in the 1980s. At that time, the concept of size quantization was formulated;[4—8] it was further developed in more recent studies.[9,10] Since then, considerable progress was achieved in this field. However, the results obtained in studies of the optical properties and in other physical experiments were difficult to interpret for long owing to polydispersity, presence of surface defects, and a low degree of crystallinity of the nanoparticles synthesized. This "backyard" was cleaned up only recently. Progress of research in this field was stimulated by the possibility of using semiconductor nanocrystals as materials for field-effect transistors, light-emitting diodes, photocatalysts, biological labels, and sensors.

As the size of semiconductor nanoparticles decreases, a threshold value characteristic of each type of semiconductors is reached. At smaller nanoparticle sizes, the energy gap (bandgap) increases and the optical spectrum is shifted toward the short-wavelength region[11] (Figs 1 and 2).

At sufficiently small size of semiconductor and metal nanoparticles (in the so-called "quantum dot" state), the density of states of conduction electrons can take only particular discrete values, which is responsible for the quantum size effect, *i.e.*, transition from a continuous to discrete energy spectrum of conduction electrons.[4,15,16]

As a result, nanoparticles possess unique optical and electronic properties not observed for corresponding bulk samples. Owing to a substantial increase in the fraction of surface atoms and to increasing role of the surface effects

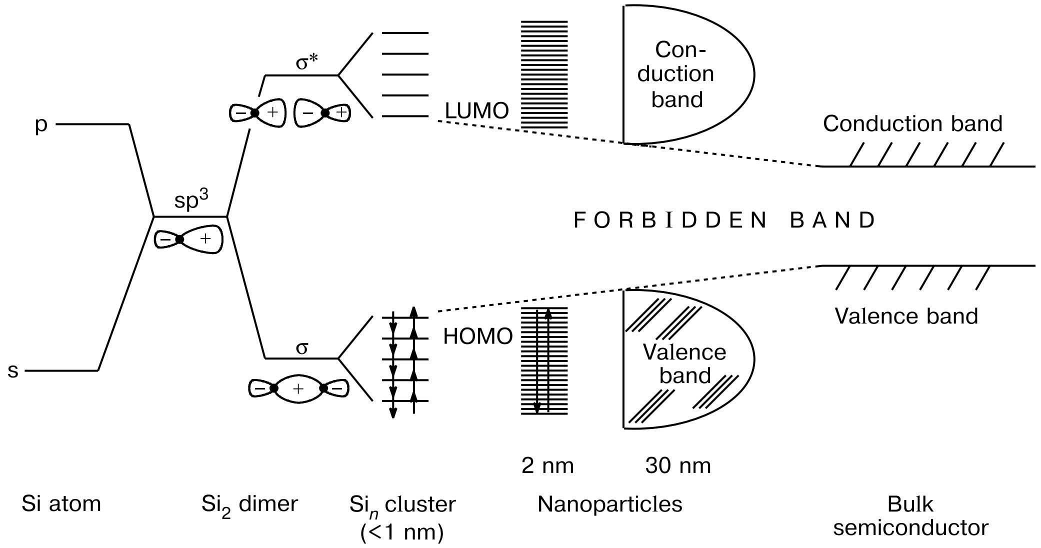

Fig. 1. Changes in the energy levels on going from Si atom to Si_n clusters, Si nanoparticles with a gradually increasing size (2 to 30 nm), and Si bulk semiconductor.[12,13]

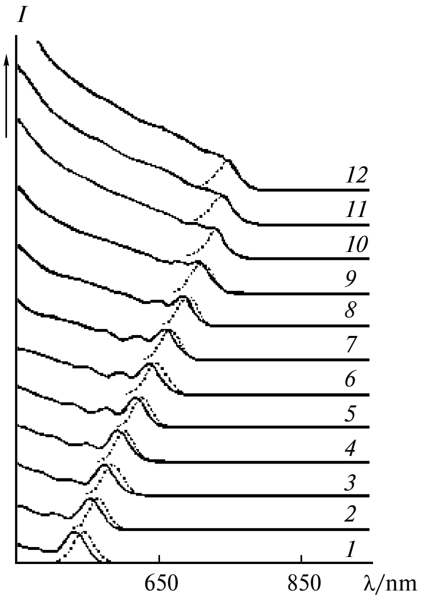

Fig. 2. Shift of absorption bands (solid curves) and photoluminescence bands (dashed lines) with an increase in the size of CdTe nanoparticles[14]: d = 3.2 (*1*), 3.3 (*2*), 3.5 (*3*), 3.6 (*4*), 3.8 (*5*), 4.2 (*6*), 4.6 (*7*), 5.3 (*8*), 6.2 (*9*), 7.7 (*10*), 8.4 (*11*), and 9.1 nm (*12*).

no only the optical properties but also other characteristics of materials (structure of electronic energy levels and transitions, electron affinity, conductivity, phase transition temperatures, *etc.*) also become dependent on the nanoparticle size and shape; these changes are usually called the "size effect". For instance, the melting temperature of semiconductor nanoparticles (*e.g.*, CdS [17,18] and GaAs [19]) decreases as the particle size decreases.*

The "quantum dot". As applied to semiconductor particles, the term "nanoparticles"** was first used in the literature only recently. Even in 1998, nanoscale CdSe particles were called[23] "colloidal particles" or "semiconductor cluster-molecules".*** Since then semiconductor nanoparticles have more and more often been called "quantum dots"* and this term has been commonly accepted.[25]

If an electron-hole pair (exciton) is formed inside a spherical particle whose diameter is equal to or smaller than the natural electron-hole separation in the material, no motion is possible for the exciton. This particle is called a "quantum dot" (QD)** because the number of degrees of freedom of the exciton is zero (0D). An exciton formed inside a particle extended in one direction (along, *e.g.*, the z axis) can not move along the x and y axes, but can move along the z axis. This one-dimensional (1D) situation is possible for nanorods, nanowires, and nanofibers. In two-dimensional (2D) nanodisks, an exciton can move along two axes.[27] It was initially assumed and then confirmed in numerous experiments that such changes in the shape of nanoparticles must affect their spectral and luminescence characteristics.[28] For instance, anisotropic rod-like CdSe semiconductor nanocrystals emit polarized light; the polarization direction coincides with the long axis of the nanorod.[29]

In the case of semiconductor nanoparticles it is quite easy to answer the question of where is the boundary between the "nano" and "non-nano" regions. This is a particle size at which the width of the energy gap becomes different from the corresponding value for compact material; in most cases this occurs at particle diameters less than 30 nm.

Nanoparticle size threshold. Taking CdS as an example, it was established that on going from compact material to nanoparticles and then to cluster molecules of the type $Cd_{32}S_{14}(SPh)_{36}\cdot 4DMF$ the bandgap (ΔE) of this semiconductor compound is gradually shifted[30] from ~2.5 to 4.5 eV. If the CdS particle size is still in the nanometer range, but ΔE = 2.5 eV, it is no longer possible to distinguish the optical characteristics of these particles from those of bulk material. Powders formed by such particles are called ultradisperse powders. In this review we leave them out of consideration.

Here, the emphasis is placed on the best studied nanoparticles, namely, chalcogenide nanoparticles and first of all, cadmium chalcogenide ones. Taking them as an example, we will analyze the main approaches and trends in progress of this field and then fragmentarily outline the available information on other types of semiconductor nanoparticles. We will leave nanostructured semiconductor materials, dense ensembles of nanoparticles, *etc.* out of consideration. The only case in point is individual nanoparticles isolated from one another in various media.

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* As it often happens, the spread of knowledge about nanoparticles and their properties among allied sciences rapidly showed that nanoscale objects are quite abundant in nature. For instance, it is known that sulfide minerals are abundant in the Earth crust; it is also believed that ZnS nanoparticles are a product of vital activity of sulfate-reducing microorganisms in zinc-enriched rocks.[20] Si nanoparticles in the interstellar space were reported.[21] More detailed treatment of the issue is presented in a monograph.[22]

** The term "nanocrystallites" is used in a more narrow sense and concerns only the nanoparticles with a well-defined (and established in some way) crystal structure.

*** Comprehensive history of these investigations is presented in a review.[24]

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* "Quantum dots" (in English-language literature); the terms "quantum sphere", "quantum crystallite", and "Q-particle" are used as synonyms.

** The fundamentals of physical approach to quantum dots are given in a book.[26]

2. Chalcogenides (sulfides, selenides, tellurides)*

The physical characteristics of this class of semiconductors vary over a rather wide range, namely, the bandgap and the Bohr exciton radius vary from 3.68 eV and 2 nm for cubic ZnS to a negative value of −0.15 eV and ~40 nm for HgTe semimetal.

2.1. Methods of synthesis

Methods of synthesis significantly influence certain characteristics of the resulting objects and play the key role on the way to success. Therefore, we will consider a number of synthetic routes to semiconductor nanoparticles.

The most important requirements for nanoparticles synthesized include a narrow size distribution, high degree of crystallinity, desired surface layer composition, and high quantum yield of luminescence. As to methods of synthesis, one must use readily available and low-toxic reagents and obtain reproducible results. Among other parameters important in applied aspect are the cost of the final products, duration of the synthetic procedure, possibility of synthesis of large amounts of products, *etc*. The aforesaid concerns methods of synthesis of all nanoparticles. In the text below we will consider the main routes to realization of these general propositions taking cadmium chalcogenide nanoparticles as an example.

The known chemical methods** of synthesis of chalcogenide nanoparticles are usually grouped[32] depending on the reagents used. Each method has its own limitations.

For instance, a yellow CdS powder can be synthesized with ease by bubbling H_2S through solutions of cadmium salts. The process was arrested[33] at the stage of nanoparticle formation by adding *p*-octylthiol and *p*-hexadecyltrimethylammonium bromide to a $CdSO_4$ solution; the CdS nanoparticles (2—10 nm) coated with alkylthiol groups were obtained by varying the reaction temperature and by dosing H_2S bubbled.

It is quite natural that researchers want to remove H_2S (and moreover H_2Se) from the list of reagents employed for the synthesis of quantum dots. Hydrogen sulfide was generated[34] *in situ* by the reaction of sulfur with tetralin at 220 °C immediately in the reaction mixture containing cadmium stearate. Adding conventional stabilizers (trioctylphosphine oxide, TOPO, or dodecanethiol) resulted in 4-nm cubic CdS nanoparticles.

Sodium salts are often used as sources of chalcogen; a typical example is provided by the synthesis of ZnS nanoparticles coated with mercaptoethanol as the stabilizing ligand.[35,36]

A simple and convenient method for the synthesis of CdS nanoparticles was proposed.[37] Here, a Cd cupferronate solution in toluene is thoroughly poured on the surface of Na_2S aqueous solution to form nanoparticles at the interface. The nanoparticle size can be to some extent controlled by varying the reagent concentrations, temperature, and duration of the reaction. It was suggested[38] that mechanochemical method for the preparation of CdS nanoparticles (4.3—8.2 nm) involving Na_2S is at least competitive with the methods based on the exchange reactions in solutions (see above).

Much more often nanoparticles were synthesized from compounds containing active sulfur (or selenium). A highly efficient method for the synthesis of the PbS, ZnS, CdS, and MnS nanoparticles of size 6—13 nm was elaborated.[39] Here, complexes of simple metal salts with oleylamine are mixed with sulfur; subsequent heating leads to formation of nanoparticles.

The choice of the starting reagents plays a significant role in obtaining monodisperse particles. $CdMe_2$ is used as cadmium source, chalcogens are delivered from their bis-trimethylsilyl derivatives $(TMS)_2E$ (E = S, Se, Te), and a mixture of trioctylphosphine (TOP) with TOPO (TOP—TOPO system) acts as a medium (solvent) for the nucleation, growth, and annealing of nanocrystallites. It is believed that this mixture of coordinating solvents plays the determining role in control of the growth and stabilization of colloidal dispersion and also passivates the surface of nanoparticles thus formed.[11] However, $CdMe_2$ is a highly toxic, pyrophoric, and expensive reagent. More environmentally friendly ("green") synthetic routes involving cadmium oxide,[40] cadmium carbonate,[41] or cadmium acetate[41,42] as Cd sources were also proposed. Using these procedures, CdSe nanocrystallites characterized by a quantum yield of luminescence of 85% at room temperature were obtained. Sulfur and selenium powders can be used as chalcogen sources to prepare cadmium chalcogenide nanoparticles by the electrochemical reduction of Cd^{2+} ion in DMSO.[43]

A promising and versatile method for the synthesis of metal sulfide nanoparticles from xanthates $(RCH_2CH_2OCS_2)_nM$ (R is hexadecyl) containing both the metal and sulfur was reported.[44] Taking cadmium salts as examples, it was shown that the technique is suitable for the synthesis of 3.5—5.2-nm quantum dots with a narrow size distribution and good spectral characteristics at relatively low temperatures (70—100 °C). Heating of $Cd(S_2CNEt_2)_2$ in hexadecylamine to 180 °C also leads to formation of CdS nanoparticles with various morphologies.[45] A versatile method for the synthesis of 4—5-nm CdS and CdSe nanoparticles by thermal decomposition

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* If necessary, in some Sections of this Chapter we analyze the results of studies on other types of semiconductor nanoparticles.

** Among physical methods of fabrication of nanoparticles, an aerosol technique[31] suitable for the synthesis of nanoparticles of different compositions seems to be the best approximation to chemical methods.

of corresponding dithiocarbamates or diselenocarbamates in TOPO at 250 °C was developed.[46]

Selenium forms stable 1 : 1 complexes with phosphines, which represent convenient selenium sources in the synthesis of metal selenides. For instance, a selenium—tributylphosphine complex was used[47] for the synthesis of PbSe nanoparticles (with Pb salts of organic acids as a lead source). Tellurium also possesses similar properties; the reaction of a Te—TOP complex with $HgBr_2$ in TOPO yields 17-nm HgTe nanoparticles.[48]

Selenium complexes with PR_3 are inappropriate for syntheses in water due to their insolubility. In these cases a Na_2SeSO_3 aqueous solution is used, which is readily formed by boiling selenium in aqueous sodium sulfite. The following reaction occurs on adding Cd salts:

$$Cd^{2+} + SeSO_3^{2-} + 2\ OH^- \rightarrow CdSe + SO_4^{2-} + H_2O.$$

Tellurium is less reactive than Se; therefore, metastable hexagonal CdTe nanoparticles (~10 nm) are synthesized[49] from cadmium stearate and Te, which slowly dissolves in TOP on heating (220 °C). The amount of dissolved Te is sufficient for gradual growth of spherical and 1D nanoparticles. To obtain aqueous colloids of CdTe nanoparticles, it is more convenient to use a freshly prepared NaHTe solution;[50] in this case (in contrast to the preceding one) only ~4-nm spherical nanoparticles with a zinc blende structure are formed. However, the quantum yield of luminescence of such particles is low (18%). A high quantum yield (65%) can be achieved using $CdMe_2$ and Te powder in a TOP—dodecylamine mixture.[51,52]

Synthesis in reverse micelles. Reverse micelles are convenient nanoreactors for the synthesis of nanoparticles of various composition.[53] Routine experiments aimed at obtaining CdS nanoparticles of a preset size[54] in inert atmosphere involve preparation of two mixtures, water—heptane and water—surfactant (sodium salt of bis(2-ethylhexyl)sulfosuccinic acid, AOT). The aqueous phase contains the necessary amounts of a Cd salt (in one solution) and sodium sulfide (in the other solution); mixing of these reagents in micelles results in the formation of nanoparticles with the desired composition and size. The method allows the size of micelles, the reagent concentration, and other parameters to be varied. The effect of the water content in reverse micelles on the size and spectral characteristics of 2-4-nm CdS nanoparticles was studied.[55]

Solvothermal method is most often used to synthesize nanoparticles with highly anisotropic shape (usually, nanorods). For instance, heating of $CdCl_2$ and S, Se or Te for 24 h in an autoclave filled with ethylenediamine (80% of the total volume) resulted in CdS, CdSe or CdTe nanorods, respectively.[56] By conducting the process over a period of 3 to 7 days one can synthesize colorless rhombohedral $CdSe \cdot 0.5en$ single crystals whose structure was established by X-ray analysis. It was shown that in this structure the CdSe networks are separated by ethylenediamine linkers.

2.2. Target variation of particle size

Luminescent and other physical characteristics are very responsive to size; therefore, methods for the synthesis of nanoparticles of preset size have been developed intensively. Possible formation mechanisms of colloids were considered[57] in relation to various factors affecting the growth of CdS nanoparticles were also studied. The results obtained are quite important for the understanding and control of processes occurring during the growth of nanoparticles.

Conventional methods for the synthesis of nanoparticles are characterized by nonuniform temperature distribution over the reaction vessel volume on heating of the reaction mixture; this leads to different conditions for the formation and growth of nanoparticles. In the case of microwave heating the whole volume is heated homogeneously and rapidly due to the interaction between the electromagnetic field and molecular dipoles; therefore, the most recent microwave-assisted methods are more and more often used in the synthesis of nanoparticles.[58] In particular, they were successfully employed[59] to obtain CdS nanoparticles of thoroughly controlled size using the $Cd(OAc)_2 \cdot 2H_2O$—thiourea system in DMF solution. It was shown that the duration of irradiation time (from a few to 40 s) affects the size of nanoparticles synthesized. For instance, the temperature of the reaction mixture increases to 353 K after irradiation for 18 s and the particle size was 2.6 nm (according to transmission electron microscopy, TEM).

Unfortunately, in some cases it is impossible to obtain nanoparticles of certain sizes. Therefore, methods for the nanoparticle size selection are elaborated. For instance, if a dispersion of CdS nanoparticles is stabilized by lyophilic coating of each particle with alkyl groups of phosphine oxide coordinated to the surface of the particle, the addition of a solvent capable of destroying this surface shielding and increasing the polarity of the medium causes precipitation, which first of all involves the largest particles. Separation of such particles by filtering off or centrifugation makes the size distributions of both the particles in solution and the precipitated particles narrower. Successive addition of MeOH to a dispersion of CdS nanoparticles 3.5 nm ±10% in size and separation of precipitate formed afforded[11] a dispersion of CdS nanoparticles with a narrower size distribution (3.7 nm ±5%). It should be noted that even so small differences in the average particle size caused the absorption spectrum of the latter dispersion to exhibit clearly seen maxima near ~400 and 530 nm (in the spectrum of the initial solution these maxima were "diffuse" due to high polydispersity). The technique allows nanoparticles of size 1.2 to 11.5 nm with a rather narrow size distribution to be prepared.[11] However, this method is labor- and time-consuming and therefore inappropriate for the synthesis of large amounts of nanoparticles.

Yet another approach involves photo-etching[60] of large nanoparticles fabricated by conventional chemical exchange methods. The method of size-selective photo-etching is based on the fact that metal chalcogenide semiconductor particles undergo photo-induced corrosion in aqueous solutions on exposure to light and that the energy band of the semiconductor nanoparticles regularly increases as the particle size decreases. When using monochromatic radiation, the wavelength is initially chosen to induce photoexcitation of the largest nanoparticles only (to cause selective photo-etching of these particles and thus to obtain smaller particles). The process is repeated at a shorter wavelength and a dispersion of progressively smaller nanoparticles is thus obtained. The observed spectral picture is similar to that shown in Fig. 2.[60] Nanoparticles with an average diameter of 1.7 nm (TEM data) were obtained at $\lambda = 365$ nm.[60] Surface stabilization of these particles by adding thiophenol led to nanoparticles structurally similar to the largest structurally characterized cluster molecule $Cd_{32}S_{14}(SPh)_{36} \cdot 4DMF$.[30]

Modern applied methods allow the synthesis of large amounts of products with narrow size distributions. Among them is the use of flow reactors. For instance, a flow microreactor with continuous spectral monitoring allows preparation of suspensions of CdS nanoparticles with preset dispersity in the range 3.2—12.0 nm.[61] The use of dosed sonication during the synthesis of ZnS nanoparticles with a narrow size distribution was reported.[62]

2.3. Methods affecting the structure of nanoparticles formed

Most often, nanoparticles freshly prepared by "solution" methods are X-ray amorphous and their crystallization usually requires an increase in the temperature of synthesis or annealing by heating a dispersion of the nanoparticles formed in a high-boiling solvent. Yet another factor that can influence the structure of nanoparticles is sonication of the reaction mixture. For instance, an increase in the duration of continuous sonication of the reaction mixture from 6 to 60 s leads to the synthesis of hexagonal crystalline rather than amorphous CdS nanoparticles.[63]

For some polymorphs with strongly different physical properties the synthesis of quantum dots with particular crystal structure is of crucial importance. A method for controlling the structure of nanoparticles formed was proposed.[64] Sphalerite-type ZnS nanoparticles were synthesized in alcohol at 120 °C over a period of 12 h. Würtzite-type ZnS nanoparticles were obtained by low-temperature synthesis of $ZnS(NH_2CH_2CH_2NH_2)_{0.5}$ complex followed by heating of the complex *in vacuo* at 500 °C for 30 min.

2.4. Nanoparticle shape control

The shape of nanoparticles is the key parameter in the design of materials possessing the anisotropy of properties (dependence on the direction along which external factors act). Nanoparticle shape control is immediately related to the understanding of processes occurring in the initial steps of the growth of a new phase under particular conditions of nanoparticle synthesis. Growth of nanoparticles in liquid media is often studied using various surfactants. It is believed[65] that they can be selectively bound to a face of the growing nanocrystallite, which makes its faces energetically inequivalent and favors nonuniform growth of different faces. By default, it is assumed that the growth of a new phase since the very early stages involves buildup of crystallographic planes rather than proceeds by the "onion" model. At the same time the smallest nanoparticles always have a spheroidal shape.

2.4.1. Quasi-1D nanoparticles

These objects are usually called "nanorods", "nanowires", or "nanofibers" — without regard to fine linguistic details. In the text below we will use only one term, namely, "nanowires". By default we will also assume that all the terms listed above become synonyms after adding the prefix "nano". Not only do nanowires possess unique electrical, optical, and mechanical properties, which offer a number of possible applications of these objects, but also serve as materials for experimental check-up of fundamental concepts used in quantum mechanics.

Recently developed methods permit particle shape control in order to obtain anisotropically shaped semiconductor nanoparticles with optimum spectral characteristics. Nanowires suitable for most applications must be crystalline and defect-free. Their diameters must range from a few to tens of nanometers (at most 100 nm) and the lengths must much exceed the diameters. The necessary length-to-diameter ratio (aspect ratio) of nanowires is specified for each given composition. For instance, a GaAs nanowire must be several times longer than the Bohr exciton radius (9—13 nm) and its diameter must lie between 2 and 13 nm. These requirements are hard to fulfill using most known methods, but attempts to meet the conditions have been made continuously, *e.g.*, the synthesis in rigid templates (in anodic alumina membranes,[66] other porous membranes,[67] carbon nanotubes[68]) and in "softer" matrices, namely, liquid crystals,[69] micelles,[70] and polymers.[71] The known methods for the synthesis of quantum dots are modified in order to obtain anisotropically shaped nanoparticles: modifications of the solvothermal method, which involves the coordinating solvents,[72] syntheses from a single precursor containing the necessary elements in a stoichiometric ratio,[45] and the so-called "vapor—liquid—solid" (VLS) method.[71]

Naturally, researchers are first of all interested in answering the question as how to perform unidirected growth of nanocrystallites in homogeneous media. To solve this problem, ethylenediamine is often used as solvent in solvothermal processes owing to high chelate-forming ability of this compound.[73—75] The CdS nanowires thus obtained have diameters (*d*) ranging from 10 to 50 nm and lengths (*l*) between 60 and 400 nm. The addition of dodecylthiol to ethylenediamine causes the formation of a material comprising bundles of nanorods of nearly the same size.[76] Longer nanowires are obtained upon adding 8-hydroxyquinoline to ethylenediamine.[77] The diameter of the nanowires remains nearly unchanged (~30 nm), while the length increases from 300 nm to 3 μm. It is important that the nanowire length is proportional to the amount of 8-hydroxyquinoline added to the reaction mixture. Later, it was established that there is no need of using bidentate ethylenediamine as the necessary component, because the CdS nanowires (d = 7—10 nm, l = 30—55 nm), as well as CdSe, ZnSe, and PbSe nanowires can be successfully synthesized in *n*-butylamine.[78] CdSe nanowires (d = 2 nm, l = 10 nm) were prepared from cadmium naphthenate and a TOP—selenium complex in hexadecylamine.[79]

Detailed studies of the nucleation and growth of aspherical CdS nanoparticles revealed[80] that the Gibbs—Thompson classical equation is inapplicable in this case and the initial stages of growth of a new phase involve formation of the so-called "magic" clusters comprised of seventeen Cd atoms.[81] The "magic" clusters are believed to be the "building blocks" for the growing anisotropic structures; conditions for the growth of particles with different shapes were established. In studies of the mechanism of directed growth of CdSe nanowires in a hexylphosphoric acid—TOPO mixture it was shown[82] that the shape of the particles formed is affected by the acid/surfactant ratio, the reagent feed rate, and duration of the reaction.

Polyethylene glycol (PEG-400) also can promote the formation of nanowires. For instance, the reaction of aqueous cadmium acetate and sodium sulfide in the presence of PEG-400 results in the formation of rod-like ($d \approx 10$ nm, $l \le 300$ nm) CdS nanoparticles.[83] Even more pronounced is the role of the polymeric environment in the formation of extended 1D structures,[84] namely, long (up to 30 μm) CdSe or CdTe nanowires are formed only in polyvinyl alcohol; otherwise, only short nanorods are formed under identical conditions.

Shape control methods of PbS nanoparticles have been elaborated.[85] The synthesis involves thermal decomposition of $Pb(S_2CNEt_2)_2$ in diphenyl ether in the presence of dodecanethiol at 230 °C and results in the formation of bead-like, star-like, cubic, and rod-like particles and their bundles. The key parameters influencing the shape of particles formed are thought to be the temperature and the duration of the reaction.

The role of the kinetic and thermodynamic factors in related processes was studied in detail.[86] It was established[86] that rather long nanowires (~5×50 nm) are formed at high concentration of the starting reagent, $Cd(S_2COEt)_2$, a reaction duration of 3 h, and at temperatures below 200 °C, whereas spherical nanoparticles are formed at a low concentration of Cd xanthogenate and a reaction duration of ~12 h. The use of coordination polymers instead of simple salts as a source of metal also favors the growth of anisotropically shaped nanoparticles under conventional solvothermal conditions.[87]

At present, general methods for the vapor-phase growth of nanowires are well developed and allow not only the composition and size of nanowires but also the crystal growth direction to be controlled. For instance, the sphalerite-type ZnS nanowires with diameters ranging from 10 to 20 nm and a few micrometers long were grown along the [111] direction.[88] The formation of long nanowires usually requires the presence of growth-"catalyst" nanoparticles (most often, readily available gold nanoparticles). Usually, the diameter of the growing nanowires is nearly 40% smaller than that of the catalyst nanoparticles. However, the use of the VLS method and gold particles requires high temperatures (500 °C) and the diameter of the resulting nanowires usually exceeds the desired value.[89,90] It was assumed that the use of metals with lower melting points (In, Bi) as "catalyst" nanoparticles will permit significant improvement of parameters of the process and the properties of particles. CdSe nanowires up to a few micrometers long with diameters ranging from 5 to 20 nm were prepared[91] from cadmium stearate and R_3PSe in TOPO at 240—300 °C using Bi nanoparticles as growth catalysts. GaAs nanowires (d = 6—17 nm) were synthesized by the "solution—liquid—solid" (SLS) method.[92] The reaction between $Bu^t{}_3Ga$ and $As(SiMe_3)_3$ was carried out in 1,3-diisopropylbenzene (b.p. 203 °C) in the presence of In nanoparticles as growth "catalysts" and a mixture of polymers of rather complex composition as stabilizer. Selenium nanowires covered with CdS nanoparticles were also obtained.[93]

Sublimation and condensation of nanoscale CdS powder can be used to obtain long CdS nanowires ($d \approx 40$ nm, l up to hundreds of micrometers) in a flow system in Ar stream over a period of 90 min.[94] A possible nanowire growth mechanism was suggested.[94] Similar results were obtained by the authors of Ref. 95. Epitaxial growth of the CdS or ZnS nanowires from the corresponding volatile compounds $M(S_2CNEt_2)_2$ using 10-nm gold nanoparticles as catalysts was reported.[96] At the same time ZnS nanowires were prepared by thermal evaporation of ZnS without any growth catalysts.[97]

Yet another possible growth mechanism of nanowires involves assembling of spheroidal primary nanoparticles along a certain direction rather than a layer-by-layer buildup of a crystallite face. For instance, conditions for the preparation of PbSe nanowires (d = 60—150 nm, l = 1—1.5 μm) from lead cyclohexanebutyrate and Se in a tributylphosphine solution were established.[47] Here, the nanowires are comprised of nearly 10-nm cubic individual nanoparticles (clearly seen in TEM micrographs) rather than anisotropic crystallites. The conductivity of a nanowire is ~7.0 $\mathrm{Ohm^{-1}\ cm^{-1}}$. There are also convincing proofs that growth of the SnS nanowires in water involves the formation of spherical nanoparticles followed by their self-assembly into nanowires.[98]

Special-purpose methods of growth of variable-composition nanowires were developed and used to obtain 1D InAs/InP,[99] GaP/GaAs and n-Si/p-Si [100] and Si/Si—Ge [101] structures.

2.4.2. Nanotubes

Nanotubes are nanowires with an internal channel passing along the entire wire. Recently, "inorganic" nanotubes have attracted considerable attention of researchers.[102—104] No general methods for the preparation of inorganic nanotubes have been developed as yet; only one more or less versatile method of synthesis of metal oxide nanotubes in organic gel was reported.[105] CdS nanotubes with a nearly 100-nm external diameter and the wall thickness ranging from 3 to 27 nm were first synthesized from $CdCl_2$ and $(NH_2)_2CS$ upon dissolution of the anodic aluminum matrix in the pores of which they were formed.[106] Considerable recent progress in this field led to preparation of not only the CdS and CdSe nanotubes [106—108] but also oxide nanotubes (TiO_2,[109] Ga_2O_3, In_2O_3,[110] ZnO [111]), and Te nanotubes.[112] It is possible to obtain different-type nanotubes in the same reactor. In this case the synthesis of Ga_2O_3 nanotubes (first stage) is followed by the change of the carrier gas from N_2 to NH_3 and subsequent synthesis of GaN nanotubes ~10 μm long with an inner diameter of 80 nm, walls 20 nm thick.[113] An interesting method for the synthesis of GaN nanotubes was reported.[114] It is based on similarity of the unit cell parameters of the würtzite ZnO and GaN. First, ZnO nanorods are grown; next, GaN layers are epitaxially deposited on them, and then ZnO is removed under the action of NH_3 at high temperature to give GaN nanotubes with the diameters between 30 and 200 nm and wall thickness ranging from 5 to 50 nm. Evaporation[115] of ZnS powder in CO + H_2 atmosphere leads to the synthesis of nanocables comprising a zinc core 20 nm in diameter and a ZnS shell 8 nm thick; subsequent evaporation of the zinc core affords ZnS nanotubes.

2.5. Growth of the surface and its effect on the properties of nanoparticles

All nanoparticles, even ultrasmall ones, are comprised of at least two fragments, the core and the shell. The shell, *i.e.*, the surface layer of nanoparticles contains the main structural defects (bond angle and bond length distortions, nonstoichiometry of composition, *etc.*) and impurities (atoms of the environment). The shell protects the core from the action of external factors and can significantly influence the physical properties of the material. In nanoparticles the proportions of the surface and inner atoms are nearly equal. As a result, the effect of the surface on the structure and optical characteristics of nanoparticles often plays the key role. In particular, the forbidden band energy in the surface layers and in the core can be strongly different owing to surface nonstoichiometry, uncompensated bonds, *etc.* It is accepted that control of the composition and structure of the surface of quantum dots plays the key role in fabrication of highly luminescent nanoparticles. By varying the properties of the surface in a directed fashion one can minimize the effect of side processes owing to elimination of non-fluorescent recombination centers.

2.5.1. Formation of surface as nanoparticle stabilization technique

Quantum dots can be stabilized by adding organic compounds, whose molecules contain long hydrocarbon radicals and terminal functional groups, to the reaction medium. Usually, these are phosphines, amines, or thiols donating an electron pair to the surface metal atoms. It is believed[116] that by varying the Cd : S ratio during the synthesis the surface of nanoparticles can be made neutral (1 : 1), positively charged (2 : 1) (Fig. 3, **A**), or negatively charged (1 : 2) (Fig. 3, **B**). The charged surface should favor the preferred sorption of corresponding charged ligands.

Ligands can not only stabilize nanoparticles but also significantly affect their spectral characteristics. This allows the absorption band and luminescence of nanoparticles of the same size to be "tuned" (within certain limits) by replacing ligands.[60] The role of the hydrocarbon radical is to block access to the surface of nanoparticles and impart it hydrophobic properties (see Fig. 3, **C**). Taking the interaction of CdSe quantum dots with dodecylamine as an example, theoretical estimation of the relative contributions of the kinetic and thermodynamic parameters to the total nanoparticle stabilization energy was

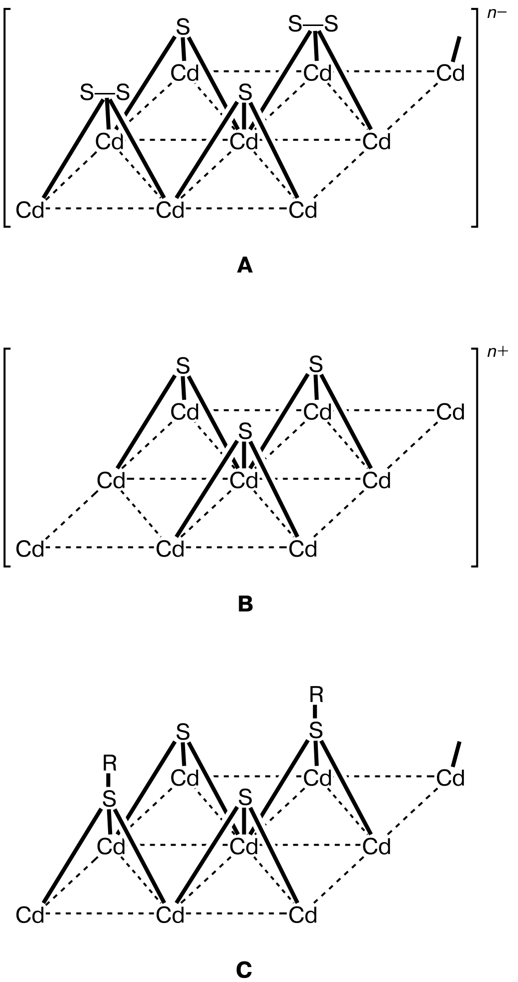


Fig. 3. Model of the surface of a CdS nanoparticle: negatively charged surface owing to the presence of excess sulfur ions (**A**), positively charged surface owing to the presence of excess cadmium ions (**B**), and surface modified by SR groups (**C**).[116]

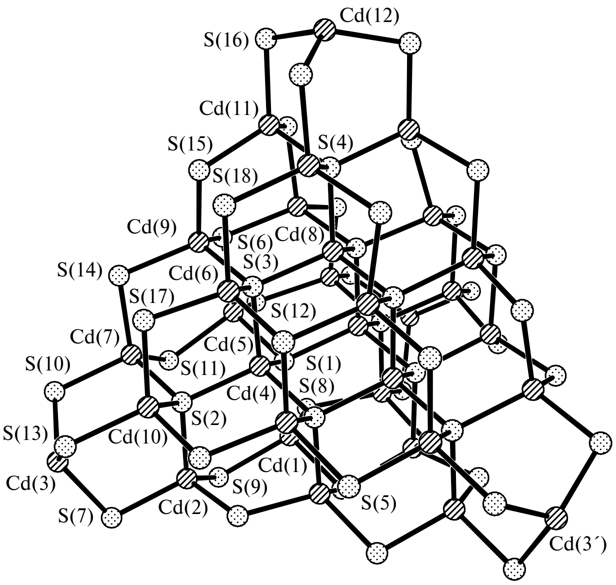


Fig. 4. $\mathrm{Cd_{32}S_{14}[SCH_2CH(Me)OH]_{36} \cdot 4H_2O}$ cluster core structure.[121] $\mathrm{CH_2CH(Me)OH}$ groups linked to each external S atom are not shown; each atom Cd(3), Cd(3´), Cd(5), and Cd(12) is bound to the O atom of the coordinated water molecule.

made.[117] It was shown that the entropy factor makes the major contribution to the interaction energy as the nanoparticle size decreases, whereas for larger particles the interaction (packing) energy between hydrocarbon chains on the surface of nanoparticles becomes significant.

Stabilizer molecules coordinated to the surface of nanoparticles also affect their solubility in organic solvents. Chemisorption of amphiphilic molecules on the surface of nanoparticles prevents their aggregation and, hence, enlargement. Thiols, polyphosphates, and the TOP—TOPO system were used as stabilizers. In some cases stabilizers behave as conventional ligands, being constituents of the surface of nanoparticles. For instance, thiols are components of CdS nanoparticles (clusters) with gradually increasing nuclearities: $\mathrm{[Cd_{10}S_4(SPh)_{16}]^{4-}}$,[118] $\mathrm{[Cd_{17}S_4(SPh)_{28}]^{2-}}$,[119] $\mathrm{Cd_{17}S_4(SCH_2CH_2OH)_{26}}$ [120] and $\mathrm{Cd_{32}S_{14}[SCH_2CH(Me)OH]_{36} \cdot 4H_2O}$,[121] $\mathrm{Cd_{32}S_{14}(SPh)_{36}(DMF)_4}$,[30] $\mathrm{Cd_{32}Se_{14}(SePh)_{36}(PPh_3)_4}$ and $\mathrm{Hg_{32}Se_{14}(SePh)_{36}(PPh_3)_4}$,[122] and a series of Cu—Se clusters.[123,124] The authors of these studies prepared single crystals of all compounds listed above and structurally charactetized them by X-ray analysis. Of course, the most difficult was to crystallize the largest cluster, $\mathrm{Cd_{32}S_{14}}$. White prismatic $\mathrm{Cd_{32}S_{14}}$ crystals about 150 μm in size are extremely unstable; because of this, they were studied being placed in a capillary containing crystals and mother liquor. Only the core atom positions (Fig. 4) were determined reliably, and it is more correctly to describe the core comprised of a total of thirteen assembled adamantane-like CdS frameworks as a tetrahedral fragment of cubic CdS lattice.

Further progress in this field permitted fabrication of a 3D superlattice (face-centered cubic lattice, fcc) from the 3.5-nm CdSe nanoparticles covered with TOPO.[125] The synthesis of pyramidal CdSe nanocrystals with a pyramid base edge of 70 nm and a height of 57 nm, built of nanoparticles 8-9 nm in size should also be pointed out.[126]

Ligand exchange is an intrinsic property of the coordination compounds and molecular clusters. It was established the stabilizer ligands on the surface of nanoparticles can be replaced by other groups using a conventional procedure based on the exchange equilibrium. The reaction was monitored by NMR spectroscopy.[127] Cleavage of S—C bonds in thiol-stabilized CdS nanoparticles was studied.[128]

2.5.2. Surface chemistry of quantum dots

A review[129] concerned with the surface chemistry of compact semiconductors is available, but the surface chemistry of nanoparticles is still in the early stage of development. At the same time, it is often necessary to modify the surface of nanoparticles. In this connection mention may be made of a target variation of the spectral and luminescence characteristics, variation of the hydrophobic-hydrophilic properties, incorporation of nanoparticles into certain matrices, binding of nanoparticles to biomolecules, and, finally, immobilization, on the surface of nanoparticles, of certain monomer units capable of incorporating nanoparticles into the growing polymer chain. Some examples are given below. The surface molecules (linkers) comprise an anchor group bound to the surface of nanoparticles and a functional group; they are separated by a chain formed by a limited number of units (spacer). Amino or thiol groups are most often used as the surface-coordinating groups in the case of sulfide and selenide nanoparticles. For instance, suspensions of TOPO-covered CdS/ZnS nanoparticles in chloroform were treated[130] with aqueous mercaptoacetic acid at pH 11; the mercapto group replaced TOPO and the particles went to the aqueous phase. Subsequent interaction with an oligomeric macroligand containing ammonium and phosphonium groups led to the reaction between them and the carboxylate anions of the surface ligands. As a result, the particles returned to the chloroform solution and were isolated in the form of a polymeric composite.

Oligomeric phosphines containing various peripheral functional groups were successfully used[131] to cover the surface of CdSe/ZnS quantum dots.

2.5.3. Core-shell quantum dots

Very recently, considerable attention has been given to nanoparticles comprised of different-composition core and shell. All shells can be divided into two types, organic and inorganic shells. The former are built of non-specific or specific ligands and have been considered above. Usually, organic ligands cause a shift of luminescence toward the long-wavelength region and do not always provide a reliable protection for the surface of nanoparticles. Often, they do not cover the whole core surface and can be involved in conventional ligand dissociation processes. Besides, the quantum yields of luminescence at room temperature are, as a rule, at most 10%.

Inorganic shells can be fabricated from a semiconductor materials whose compositions differ from the core composition or from a metal. Usually, inorganic shells are more stable to chemical degradation or photooxidation than organic ones.

One of the main goals of studies on the preparation of the core-shell quantum dots is to obtain systems with holes confined mainly in the core and electrons mainly delocalized over the shell. 1s—1s-Electronic transitions in spherical quantum dots covered with a different-type semiconductor were calculated.[132] The greatest difficulty in the experiments concerning creation of core-shell quantum dots is to prove the composition and structure of the nanoparticles formed.

Metal coatings are still rare. Methods of coverage of ZnO nanoparticles with gold or platinum and the emission characteristics of such particles were analyzed.[133] "Platination" of CdS nanoparticles and their catalytic activity were reported,[134] but the structure of the particles was not reliably established in that study.

Semiconductor—semiconductor systems. The battle for increase in the quantum yield of luminescence required design of core-shell and more complex nanoparticles.

Consider the so-called "nanoheterostructures",[24] *i.e.*, core-shell quantum dots where the core and the shell are two different semiconductor materials with different energy band structures. Two possible cases are shown in Fig. 5.

Most experiments were carried out using the CdSe—CdS system[135] with the würtzite structure of both components whose unit cell volumes differ by 3.9% only; this is sufficient for epitaxial growth and at the same time precludes alloying of components. The forbidden band energy difference is large enough to provide an increase in the quantum yield of luminescence with an increase in the shell size; this simultaneously makes the particle core more stable. At present, the most promising method of shell buildup by deposition of cations and anions on the surface of nanoparticles seems to be the Successive Ion Layer Adsorption and Reaction (SILAR) approach,[136] which was, in particular, used to produce large amounts

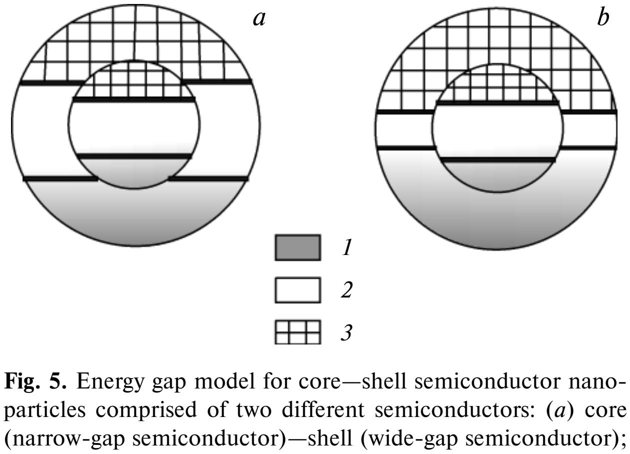


Fig. 5. Energy gap model for core—shell semiconductor nanoparticles comprised of two different semiconductors: (*a*) core (narrow-gap semiconductor)—shell (wide-gap semiconductor); (*b*) core (wide-gap semiconductor)—shell (narrow-gap semiconductor).[24] Valence band (*1*), forbidden band (*2*), and conduction band (*3*).

of monodisperse CdS—CdS nanoparticles.[137] In this case the SILAR method involved successive introduction of a precursor giving a Cd layer on the surface of CdS nanoparticles and then a precursor forming an S layer on the formed Cd monolayer into the solution. The amounts of the Cd and S precursors, necessary to form the first and each subsequent monolayer, were determined by the number of surface atoms in the layer. The average thickness of the CdS monolayer was accepted to be 0.35 nm; the buildup of a monolayer increased the particle diameter by 0.7 nm. The synthesis was performed in an octadecene—octadecylamine mixture in Ar atmosphere at 240 °C with cadmium oxide and elemental sulfur as sources of Cd and S, respectively. Using this method, one can obtain[137] a few grammes of CdSe—CdS nanoparticles with the desired number of layers. A rather simple one-step method of production of highly luminescent CdSe—CdS nanocrystallites (quantum yield ~80%) was elaborated.[138] Methods for controllable-size growth of ZnS [139,140] (epitaxial growth), CdS [135] or ZnSe [141] (solvothermal method) shells on the surface of the CdS nanoparticles were proposed. This not only increases the efficiency of photoluminescence but also improves the stability of photocharacteristics and the chemical stability of nanoparticles. However, the lattice parameter difference between, *e,g,*, CdSe and ZnS (~12%) can produce defects in the shell (especially, in a thin shell).

The addition of 3-mercaptopropyltrimethoxyxilane to a toluene solution of the di(2-ethylhexyl)sulfosuccinate-stabilized CdS nanoparticles was reported;[142] the former compound replaced the stabilizer molecules on the surface of nanoparticles. Dropwise addition of water to the boiling solution resulted in precipitation of CdS nanoparticles covered with SiO_2 with a core : shell size ratio of 5.0 : 5.2. This short communication also concerned the methods suitable for answering the question of the structure of these complex nanoparticles.

The luminescent characteristics of the CdS/HgS [24] and CdS/PbS [143] core-shell nanoparticles and CdS/HgS/CdS three-layer nanoparticles.[24] were obtained and studied. CdTe/CdSe and CdSe/ZnTe nanoparticles were synthesized[144] by the methods mentioned above. The possibility of control of charge carrier distribution inside the quantum dots was demonstrated. A controlled fabrication and structural characterization of CdSe/CdS/ZnS three-layer nanoparticles was reported.[145] In order to incorporate nanoparticles into biological objects, one should synthesize water-soluble core-shell nanoparticles, which was done[146] taking CdSe/ZnS nanoparticles as an example using an alkylcarboxylic acid with two SH groups bound to the surface of nanoparticles as ligand.

The next step toward improvement of stability and an increase in the quantum yield of quantum dot luminescence involved elaboration of shape control methods for complex nanoparticles. The possibility of selective nucleation and epitaxial growth of a different material on a particular crystallographic face of the core was demonstrated.[147] This allowed the shape of the growing semiconductor heterostructures to be controlled by combining a spherical 0D CdSe core with a rod-like 1D CdS shell, which led to considerable increase in the quantum yield of luminescence.

A semiconductor—semiconductor nanoparticle system can be represented as a solid solution of two chalcogenides; such nanoparticles exhibit a higher efficiency of luminescence. For instance, $Zn_xCd_{1-x}Se$ ($0.28 < x < 0.67$) nanoparticles 5.8—7.5 nm in size[148] are characterized by a systematic shift of the emission peak toward the short-wavelength region (quantum efficiency of 70—85%). Similar results were obtained for CdSeS particles ~5 nm in size.[149]

2.6. Organized quantum dot nanostructures

2.6.1. Quantum dots on substrates

Planar technology still dominates in production of electronic devices. Therefore, formation of organized planar ensembles of nanoparticles and nanowires on the surface of various substrates and electrode systems is a topical problem. The possibilities of the molecular epitaxy and MOCVD (Metal Organic Chemical Vapor Deporsition) methods for fabrication of nano-island quantum dot films were demonstrated[150] taking InGaAs/AlGaAs diode lasers as examples.

Recently developed chemical methods are also efficient in this respect. For instance, coverage of a smooth surface of a gold substrate with 1,6-hexanedithiol or 1,10-decanedithiol led to formation of self-assembled monolayers.[151] Immersion of the substrate into a suspension of the CdS nanoparticles ~3 nm in size prepared by conventional technique in reverse micelles and stabilized with sodium bis(2-ethylhexyl)sulfosuccinate led to formation of a monolayer of CdS nanoparticles. Further addition of dithiol gave more complex layer-by-layer structures.[151] Interesting phenomena were observed[152] upon coverage of an oxidized surface of a silicon wafer with CdS nanoparticles 10 nm in size. Nanoparticles self-organized on annealing at 850 °C and formed concentric circles ($d \leq 1$ μm) comprised of individual nanoparticles, which retained the luminescent properties.

Layer-by-layer alternate adsorption was employed to fabricate biosensors containing incorporated quantum dots.[153] In order to design nanocomposite photorefractive materials, an ITO (indium tin oxide) wafer was coated[154] with a solution containing poly(*N*-vinylcarbazole) with some additives and mercury acetate. After removal of the solvent the sample was kept in H_2S atmosphere and then heated *in vacuo* to remove volatile products. The authors[154] stated that they first obtained a material containing narrow-gap HgS semiconductor nanoparticles (~50 nm in size) in the photorefractive polymer matrix, which can operate in the IR telecommunication region (at 1.31 μm). Studies on the synthesis of CdSe, CdTe, and TiO_2 nanoparticles on the surface of carbon nanotubes should also be pointed out.[155]

2.6.2. Quantum dots in Langmuir—Blodgett films

Langmuir—Blodgett films are often used for preparation of organized quantum dot nanostructures. For instance, CdS nanoparticles 2.5—5.0 nm in size are formed in a fatty acid monolayer from a cadmium salt of the same acid and dodecanethiol;[156,157] PbS and other metal sulfide nanoparticles were synthesized from the corresponding salts.[158—160] Often, sulfide nanoparticles are synthesized by exposure of films to H_2S atmosphere.[161—165] Multilayer composite Langmuir—Blodgett films containing CdS nanoparticles and conducting polymers were obtained.[166] However, semiconductor (in particular, CdS and PbS) nanoparticles synthesized in multilayer planar molecular "nanoreactors" — Langmuir—Blodgett films — are often characterized by a rather large size dispersion and shape anisotropy. The possibility of efficient shape control of the semiconductor nanoparticles produced by this method is doubtful. Besides, stabilization of nanoparticles in the film matrix makes further manipulation of the particles difficult. These reasons are responsible for a relatively limited use of that technique for the synthesis of semiconductor nanoparticles.

2.6.3. Quantum dots in inorganic matrices

The size of the inner cavities of most zeolites permits the synthesis and stabilization of nanoparticles at most 1 nm in diameter; so small nanoparticles can hardly be obtained and stabilized by other methods. A detailed study of the methods of synthesis and spectral characteristics of CdS and PbS nanoparticles in a number of zeolite matrices and in porous glass was carried out.[167] It was shown that zeolites restrict the particle size to 1 nm, whereas the use of porous glass allows a possible particle size to be increased to 4 nm. Ion exchange followed by bubbling H_2S through the zeolite Y matrix yielded[168] isolated CdS and PbS nanoparticles less than ‹1.3 nm in size.

Mesoporous silica gel (usually, SBA-15 comprised of hexagonally arranged nanotubes of diameter 9 nm)[169] is often used as a matrix for the synthesis and stabilization of 1D nanoparticles of different compositions. For instance, CdS nanoparticles were bonded to Zn atoms of Zn-doped SBA-15 (pore diameter ~6 nm) through dithiol bridges.[170] Samples thus obtained exhibited a high photocatalytic activity. CdS nanostructures can also be formed inside SBA-15 pores by impregnating the mesoporous silica with aqueous cadmium thioglycolate and subsequent annealing at 160 °C for 24 h.[171] Dissolution of SiO_2 in 2 *M* NaOH affords a material comprised of CdS nanowires of diameter 6 nm with a ~3 nm separation between wires. CdS, CdSe, In_2Se_3, PbS, HgSe, Bi_2S_3, and AgI nanoparticles can be incorporated into silicate glass with retention of the main spectral characteristics and luminescent properties.[172] Highly luminescent samples were fabriced by incorporating CdTe nanoparticles during the synthesis of glass in the sol-gel process.[173]

2.6.4. Quantum dots in polymers

It is believed that only creation of quantum dot assemblies evenly distributed over the polymer matrix and isolated from one another can help realization of their potential unique photoluminescence properties;[174,175] this also must be favored by good mechanical characteristics and optical properties of polymers.[176] However, research in this field faces many problems.

The main problem is to retain the high luminescent characteristics of the initial nanoparticles in the course of monomer coordination on the surface of quantum dots and subsequent polymerization; unfortunately, it does not always happen.[177] In particular, an attempt to obtain CdS nanoparticles within a Nafion membrane film failed, because the spectral characteristics of the nanoparticles appeared to be identical to those of compact CdS.[178] These difficulties can be avoided.[179] First, CdTe nanoparticles 2.8, 3.3, 3.6, and 4.0 nm in size were obtained in the reaction of $CdCl_2$ with NaHTe in water in the presence of a stabilizer (3-mercaptocarboxylic acid). Next, a specific surfactant, octadecyl-*p*-vinylbenzyldimethylammoniym chloride, was synthesized. Using a styrene solution of this surfactant, CdTe nanoparticles were completely extracted from the aqueous phase, thus replacing 3-mercaptocarboxylic acid. Polymerization of the styrene solution under conventional conditions resulted in centimeter-sized rod-like nanocomposites, which can luminesce in the spectral regions from orange to green depending on the size of the incorporated CdTe nanoparticles.

In some cases polymerization is carried out using nanoparticles as initiators. For instance, CdS nanoparticles on the surface of SiO_2 nanogranules were modified[180] with a radical polymerization initiator and then polymerization of methyl methacrylate was carried out. A solution of the polymer containing nanoparticles was poured on the substrate and, after removal of the solvent, the spectral characteristics of nanoparticles were studied. But more often, classical polymerization initiators are employed. The synthesis of CdS nanoparticles from $CdCl_2$ and NH_2CSNH_2 and polymerization of acrylamide (with

2,2´-azobis(isobutyronitrile) as initiator) in an autoclave at 140 °C over a period of 12 h were carried out simultaneously.[181] A composite thus obtained contained the CdS nanoparticles ~7 nm in size, while the corresponding reactions involving ZnS and PbS performed under identical conditions produced larger nanoparticles. In block copolymers, nanoparticles are grouped within certain domains rather than evenly distributed over the entire volume of the polymer, thus forming materials with microdomain morphology.[182] Ligand-coated 2-nm CdS nanoparticles can be linked to one another by multiple *p*-xylylene groups to give a polymer containing uniformly distributed nanoparticles.[183]

In the text above we considered the incorporation of quantum dots into polymers during polymerization of certain monomers; however, polymers themselves can also be used for this purpose. For instance, polystyrene and *n*-dodecyl mercaptan stabilized CdS nanoparticles 6.3 nm in size were dispersed[184] by sonication in $CHCl_3$; the dispersion formed was poured onto substrate at room temperature. The spectral characteristics of the film thus obtained corresponded to the expected values (see Ref. 185). Layer-by-layer assembly of hybrid films formed by the CdS nanoparticles and poly(vinylpyridine) molecules was also reported.[186]

Layer-by-layer alternate adsorption of the polycation (poly(diallylmethylammonium chloride)) molecules and negatively charged semiconductor nanoparticles (CdS, PbS, TiO_2) was successfully used to form ultrathin composite films.[187] This technique was also employed to prepare highly luminescent CdTe/polycation films on solid substrates[188] and films containing incorporated CdS nanoparticles covered with poly(acrylic acid).[189]

Composite films containing quantum dots and polyelectrolytes were obtained using a combined approach involving layer-by-layer alternate adsorption of unlikely charged film components and the Langmuir—Scheffer method.[190]

Of particular interest are studies in which nanoparticles are incorporated into the polymers that can not only act as matrices but also possess certain functional characteristics, namely, electrical conductivity, spectral, and magnetic characteristics. Polyaniline is one of the most widely used conducting polymers. A polyaniline-based material containing ~10-nm TiO_2 nanoparticles (nanotubes with diameters ranging from 90 to 130 nm) was obtained.[191] Design of materials for light-emitting diodes involved the synthesis[192] of stabilized InAs/ZnSe core-shell nanoparticles (4.8 and 1.5 nm in size, respectively) with intense photo-emission near 1.3 μm followed by mixing with a polymer solution in a toluene solution. The film obtained after removal of the solvent exhibited good functional characteristics (luminescence efficiency of ~0.5%).

Considerable attention has been given to preparation of polymeric nanocomposites with high refractive index.[193] Nanoparticles 2—5 nm in size covered with 4-thiomethylstyrene were introduced[194] into a solution in which polymerization of an urethane-methacrylate monomer was performed simultaneously. This resulted in a composite film containing evenly distributed nanoparticles, which is highly transparent in the visible region, and has a high refractive index. CdS quantum dots were incorporated into a poly(acrylic acid) film.[195]

The Langmuir technology was used to synthesize planar complexes of DNA and an amphiphilic water insoluble polycation (alkylated polyvinylpyridine derivative), which were then used for the synthesis of CdS nanoparticles.[196] This gave stable ultrathin polymeric nanocomposite films containing the amphiphilic polycation, DNA molecules, and organized quasi-linear ensembles of semiconductor nanoparticles as structure constituents.[197,198] The same immobilized planar DNA—amphiphilic polycation complexes were used to obtain organized nanostructures comprised of CdSe nanorods (d = 4 nm, l = 25 nm)[199] (Fig. 6). Complexes of DNA with CdSe cationic nanorods belong to a novel class of highly organized bioinorganic nanostructures in which luminescent semiconductor nanorods form oriented collinear structures nearly 1 μm long. It was found[200] that the formation of organized complexes DNA/CdSe nanorods depends on the reaction duration and on the concentration of nanorods in a complex fashion.

In the text above we presented a number of examples of polymeric materials containing incorporated nanoparticles. At the same time, polymers are often used only as thin (sometimes, monolayer) coatings on the surface of nanoparticles: polyvinyl alcohol—CdSe nanoparticles 4.3 nm in size;[201] PbS rods (10×250 nm) coated with poly-

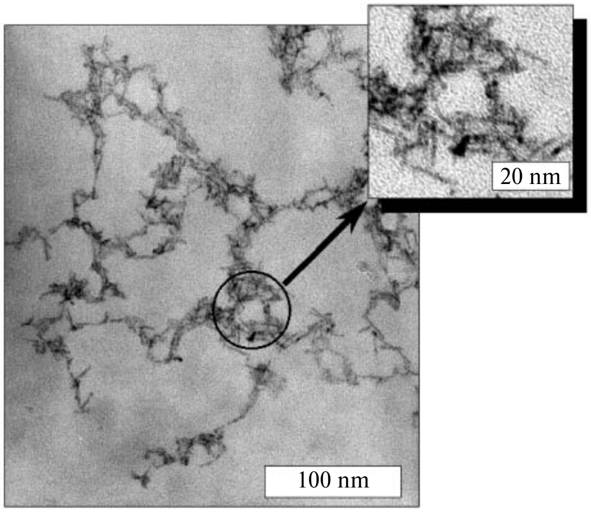


Fig. 6. Electron micrograph of CdSe nanorods incorporated into DNA—amphiphilic polycation planar complexes; the inset shows a part of the image (magnified) to demonstrate individual nanorods.[199]

vinyl acetate 5 nm in size,[202] and CdSe nanoparticles coated with poly(amidoamino) dendrimers.[203]

2.7. Determination of the size, composition, and structure of quantum dots

In determining the structure of quantum dots researchers face the same methodological problems as those posed in the case of metal nanoparticles. The particle size is most often determined using TEM and its modification, high resolution TEM (HRTEM). The possibilities of modern methods, as applied to nanotechnology problems, have been analyzed in a review.[204] In some cases the small-angle X-ray scattering (SAXS) and EXAFS methods are employed (see a review[24]). X-Ray phase analysis data are presented in most studies but do not serve as the only source of reliable information; usually, the results obtained are confirmed by other structural methods. Some examples are given below. The size and size distribution of the same nanoparticles obtained by different methods were compared in a number of studies; the results obtained are in good agreement. For instance, the size of ZnS nanoparticles is 2.8±0.2 nm from the absorption edge in the visible and UV spectra, 3.0±0.3 nm according to TEM data, and 1.4 nm according to X-ray phase analysis data (based on the Debye—Scherer relation).[205] A similar study of ZnO nanoparticles was also reported.[206]

The methods listed above are used in studies of nanoparticles of all compositions. Specific methods employed in the studies of quantum dots include NMR of ligands, EPR, absorption and emission spectra of nanoparticle solutions, pulsed photolysis and pulsed radiolysis, Auger spectroscopy, mass spectrometry, nonlinear optics methods, photoelectron spectroscopy, *etc.*

Often, the core and the shell structures are determined using different approaches and somewhat different methods. The composition, structure and, often, the crystal structure of the core nanoparticles have been studied much better than the surface of these objects. At the same time the surface of nanoparticles plays an important role in the determination of their structural, thermodynamic, optical, magnetic, and transport properties. Moreover, taking the ZnS nanoparticles 3 nm in size as an example, it was reliably proved[205] that so small change in the composition of the surface as the surface sorption or desorption of methanol or replacement of methanol by water causes a measurable (using EXAFS) reversible change in the core structure from disordered to sphalerite-like one. Due to low symmetry of atomic environment and the absence of long-range order in the surface layer conventional methods for determination of the surface structure are little informative in this case. X-Ray photoelectron spectra of different-size CdSe nanoparticles on a gold substrate were measured[207] and it was shown that access to all surface Cd atoms was blocked by TOPO, whereas Se atoms were free and oxidized on exposure to air, thus forming a SeO_2 surface layer. In contrast to this, neither Cd nor Se were passivated in pyridine and both types of surface atoms oxidized being exposed to air.

2.8. Optical properties

Detailed consideration of the spectral characteristics and specific features of quantum dot luminescence goes beyond the scope of this review. The readers are addressed to comprehensive reviews.[27,208—211]

Manifestation of the quantum size effects in the optical characteristics of semiconductor nanoparticles has been extensively studied for long.[212—214] Efficient methods for theoretical description of the system of electronic energy levels and their transformation as a result of the quantum size effects in semiconductor nanoparticles have been elaborated.[208,215—217] Among disperse semiconductors, of particular interest are nanoparticles 2—20 nm in diameter, because it is this size range in which the major changes in the electronic and spectral characteristics compared to the corresponding bulk materials are observed (see a review[218]).

The CdS absorption bands are shifted as the particle size varies;[219] a typical picture was reported in Ref. 11. Nanoparticles larger than 6 nm (*i.e.*, larger than the exciton radius in compact material) exhibit efficient absorption at ~515 nm, which corresponds to a photon energy of ~2.4 eV, which corresponds to the bandgap in compact CdS. As the particle size decreases, the absorption edge is shifted toward the short-wavelength region so that the CdS particles smaller than 2.2 nm become colorless. However, at a particle size of less than 1 nm the absorption peak is shifted to 280 nm and no emission is observed even at 4.2 K.[168] As the particle size decreases, the absorption spectrum is structurized (maxima and shoulders appear). Particle size variation also affects the lifetime of luminescence.[220]

A review of the spectral features of individual CdSe nanoparticles has been reported.[221] The absorption spectra of CdSe nanoparticles were measured[11] and the shift of the absorption maximum depending on the particle size randing from 1.2 to 11.5 nm (100—30000 atoms per particle) was monitored. As the particle size, the maximum is regularly shifted toward the long-wavelength spectral region but does not reach a value typical of bulk material (716 nm) even for the largest particles. According to calculations, in this case the energy gap (energy difference between the highest occupied and lowest unoccupied MOs, HOMO and LUMO)) gradually changes by more that 1 eV.

In the early studies the quantum yields of luminescence of CdS nanoparticles were at most 1%. The low efficiency of luminescence was attributed to the fact that the CdS quantum dots had defects suitable for nonradiative recombination of charge carriers. Detailed surface "quality" analysis of CdSe, CdTe, and InAs nanoparticles and of the effect of surface on the efficiency of photoluminescence of certain fractions of nanoparticles with a narrow size distribution was carried out.[222] It was possible to manipulate defects in the surface layer (and, hence, the efficiency of luminescence) by varying the nature of ligands, solvent, matrix, *etc*. The authors of the early studies[223,224] pointed to considerable increase in the quantum yield upon introduction of small amounts of alkylamines into solutions of CdS nanoparticles. The CdS nanoparticles 4—6 nm in size were "activated" by covering their surfaces with cadmium hydroxide, which led to an increase in the quantum yield to more than 50%.[214] Analogously, "passivation" of the surface of CdTe nanoparticles with thioglycolic acid was responsible for considerable increase in the quantum yield of photoluminescence.[116] *p*-Phenylenediamine, a well-known hole acceptor, efficiently traps photogenerated holes on the surface of CdSe quantum dots.[225]

Along with changes in the particle size the factors mentioned above affect the shape of the fluorescence spectrum, *i.e.*, the change in the color of the emitted light (see also Ref. 226). A review[24] of the results of single-quantum-dot luminescence measurements is available.

The change in the shape of nanoscale objects on going from quantum dots to nanowires causes removal of energy level degeneracy characteristic of spherical nanoparticles and separation of the absorption and emission peaks, which is of great importance for such applied aspects of optoelectronics as fabrication of light-emitting diodes or quantum dot lasers. In the case of CdSe nanoparticles the HOMO is mainly composed of the Se 4p-AOs, whereas the major contribution to the LUMO comes from Cd 5s-AO. From the simplest orbital symmetry considerations it follows that the spherical Cd s-orbitals and Se $p_{x,y}$-orbitals are much less responsive to the 0D → 1D transition and to changes in the length of nanowires. Semiempirical calculations[227] of the electronic structure of CdSe nanowires carried out by the pseudopotential method with variation of nanowire length showed that extension of the system causes discrete energy levels to merge into a single energy level, *i.e.*, the situation approaches that characteristic of a compact material. It was theoretically shown[228,229] that variation of the shape of nanoparticles causes not only changes in the structure of electronic energy levels but also influences the formation of the surface states. The motion of excitons across the surface along the long axis of ellipsoidal nanoparticles or (which is better) nanorods is less hindered than in the case of spherical nanoparticles. As a result, CdSe nanorods emit polarized light even at room temperature.[29]

Photocatalysis. The photocatalytic activity of CdS nanoparticles (3.7—5.1 nm in size) connected to zinc-modified SiO_2 nanogranules *via* dithiols (dt) was studied.[230] It was shown that H_2 release from aqueous solution of isopropyl alcohol upon UV irradiation is maximum when the CdS—dt—Zn—SiO_2 system is used as catalyst. This effect was explained by electron transfer from a more readily photoexcited ZnS (S atom of dt) to CdS nanoparticles, whereas isopropyl alcohol is an electron donor, which blocks access to holes formed upon photoexcitation of CdS. Specific features of photooxidation-induced luminescence were also studied.[231,232]

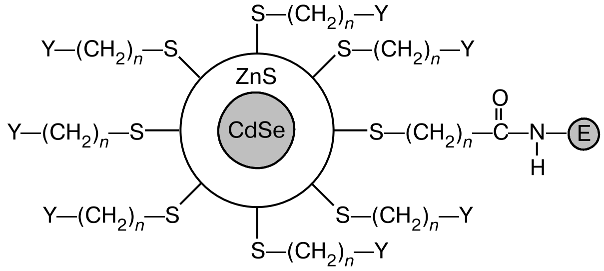
2.9. Quantum dots in biochemical and medical research

The unique photophysical properties of chalcogenide quantum dots allow them to be used as efficient fluorescent labels or photoelectrochemical tests for various biomedical applications. The development of this avenue of research is due to not only the quantum size effects but also the fact that the average sizes of nanoparticles used are comparable with the size of biomacromolecules. This consistence between the characteristic sizes opens prospects for practical applications of semiconductor nanoparticles in biomedical technologies and provides an example of integration of nanotechnology and biology. In the future, this can lead to emergence of nanobiotechnology, a novel field of high-efficiency and great-practical-value research. At present, investigations using quantum dots led to some advances in diagnosis, directed therapy, and molecular and cell biology.

To this end, various quantum dot bioconjugates were prepared. In some cases CdSe nanoparticles can be used instead of fluoresecent dyes in the visualization of biological objects.[233,234] Energy transfer between quantum dots (donors) and proteins containing fluorescent labels (acceptors) was studied in detail.[235] In addition to *in vitro* "grafting" of quantum dots to cell structures[236,237] the possibility of using semiconductor nanoparticles for *in vivo* visualization of individual structures was demonstrated.[238,239] Going this way, researchers faced a number of problems. In particular, aggregation of nanoparticles was often observed owing to high surface activity of nanoparticles and a weak interaction between them and biomolecules in freshly prepared specimens. Besides, methods of synthesis of nanoparticles were too complex and poorly reproducible; often, syntheses were carried out in organic solvents and the transition to aqueous media was problematic.

Semicondustor nanoparticles (1.3 nm CdS) stable in water were obtained using tripeptide glutathione as the surface ligand.[240]

Elimination of these problems involves the synthesis of quantum dots immediately inside biomolecules. For



Y = COOH, SH, NH_2; *n* = 1—10; E — protein.

Fig. 7. Model for surface modification of a core-shell nanoparticle by $HS(CH_2)_n$—Y linkers; a possible type of linker—protein amino group binding is shown on the right.[244]

instance, a biopolymer chitozan was used[241] as a matrix for the synthesis and stabilization of CdS nanoparticles 4.2 nm in size (chitozan exhibits some attractive properties, namely, it is hydrophilic, biocompatible and biodegradable, and also possesses a protein and DNA affinity.) Besides, the binding of CdS nanoparticles with phosphorothioate oligonucleotide was established.[242]

Mercaptopropionic acid stabilized CdSe/ZnS core-shell nanoparticles 4.2 nm in size were modified[243] with an oligonucleotide containing a thiolate group and used then as fluorescent labels in the studies of reactions involving DNA (Fig. 7). The same quantum dot system stabilized with mercaptopropionic acid can be covalently linked to biomolecules (*e.g.*, transferrin) and successfully used for recognition of specific antibodies or antigenes.[244]

Magnetic luminescent nanocomposite nanoparticles with the magnetic core (superparamagnetic Fe_2O_3 nanoparticle stabilized by a polymer layer) covered with adsorbed monolayer of CdSe/ZnS quantum dots were synthesized.[245] Combination of the properties of such nanostructures allows them to be employed in various bioanalytical methods including luminescent sensorics and magnetic separation. The possibilities were demonstrated of using such magnetic-luminescent composite nanoparticles for the detection of malignant cells. The functionalized CdS nanoparticles were used as fluorescent labels for DNA detection and determination.[246] Chemisorption of proteins on the surface of quantum dots was analyzed.[247,248] The results of studies on the design of hybrid functional devices based on proteins and nanoparticles with different compositions were collected in a review.[249]

It is quite natural that the problem of toxicity of semiconductor nanoparticles posed immediately after the start of investigations aimed at their immobilization on biological objects *in vitro* and the more so *in vivo*. It was hard to expect that incorporation of so toxic elements as Cd or Te into biological objects will cause no response in organism(s). *In vitro* cytotoxicity of CdSe quantum dots to hepatocites was studied.[250] Toxicity of the objects under study was established with certainty and it was shown that its intensity is proportional to the amount of free Cd^{2+} ions produced owing to partial destruction of the CdSe surface. At the same time it was established that coverage of nanoparticles with, *e.g.*, ZnS monolayers significantly reduces the toxicity. Thus, in each particular case research and development must be accompanied by performing thorough toxicity tests.

3. Nitrides, phosphides, arsenides

Compared to chalcogenide nanoparticles, semiconductor nanoparticles of the $A^{III}B^{V}$ type have been much poorer studied. They luminesce in the interval between the near IR (InAs) and blue (GaN) regions and can find a broad spectrum of applications. $A^{III}B^{V}$-type semiconductor nanoparticles are rather large compared to $A^{II}B^{VI}$ ones, but large Bohr exciton radius allows them to retain the quantum properties.[251] However, $A^{III}B^{V}$ nanoparticles and nanofibers synthesized in the early studies were unacceptably large (long) and highly polydisperse.[252,253] This was due to the lack of corresponding precursors and to problems in the crystallization of $A^{III}B^{V}$ semiconductor nanoparticles at temperatures below 400 °C owing to high bond covalencies in these compounds.

Gallium nitride GaN belongs to the most important semiconductors. The emphasis is placed on fabrication of nanorods, nanowires, nanotubes, and other 1D nanostructures including nanocomposite structures based on GaN using arc discharge,[254] laser vaporization,[255] sublimation and pyrolysis,[256,257] and the CVD method.[258,259] A version of the CVD technique was used[260] to obtain single-crystalline würtzite GaN nanowires (*d* = 50—60 nm) hundreds of micrometers long. GaN nanowires with diameters ranging from 15 to 60 nm can be prepared from Ga acetylacetonate and NH_3 at 620—750 °C.[261] Thermal CVD method was employed to synthesize large amounts of GaN nanowires (*d* = 30 nm, up to 1 mm long) on Fe nanoparticles and to simultaneously obtain GaN nanowires covered with graphitized BCN layers.[262] GaN nanorods can also be efficiently covered with graphitized carbon layers. Si-doped (3%) GaN nanowires were fabricated.[263]

Aluminum nitride. Stability of AlN nanotubes was predicted theoretically;[264] the material was obtained[265] by the action of NH_3—N_2 mixture on Al powder impregnated with a small amount of cobalt sulfate (1 mmol per g of Al) at 1100 °C. It was suggested that these nanotubes (*d* = 30—80 nm), which can be up to a few micrometers long, are an excellent substrate for growth of GaN layers (the lattice parameters differ by 2% only) in order to fabricate heterostructures for nanoelectronics.

Gallium arsenide GaAs also belongs to the most important semiconductors. It is widely used in optoelectronic devices and solar cells. GaAs nanoparticles are obtained in a variety of fashions,[19,266—269] the particles having a slightly extended shape (the ratio of radii is 1.2 to 1.3) and containing an excess amount of Ga (5 : 4) compared to the stoichiometric composition. GaAs nanoparticles 4.4—6.2 nm in size were also obtained from $GaCl_3$ and $As(NMe_2)_3$ in 4-ethylpyridine.[270] GaAs nanowires were grown[271] by molecular epitaxy.

Gallium phosphide GaP is a widely used wide-gap, thermally stable semiconductor material ($\Delta E = 2.26$ eV). GaP quantum dots and nanowires were prepared[272] by thermal decomposition of specially synthesized precursor $Ga(PBu^t{}_2)_3$ in amines. This method permits the synthesis of monodisperse nanoparticles with identical shape. GaP nanowires ($d = 40$ nm, $l \le 300$ μm) were grown on nickel nanoparticles as "catalysts" by sublimation of GaP powder.[273] The optical properties of GaP nanowires ($d =$ 20—50 nm) were studied.[274]

Indium phosphide InP is of interest as a material for fiber optics. InP nanowires grown in the presence of nanocatalysts can be used as sensitive 1D photodetectors.[275] or light-emitting diodes.[100] InP quantum dots were synthesized and their photoluminescence was studied in detail.[276] InP nanorods ($d = 20$—25 nm, $l = 700$ nm) with vertical orientation were grown by metal-organic vapor-phase epitaxy on a substrate using gold nanoparticles as "catalysts".[277]

4. Oxides

Indium oxide In_2O_3 is a transparent n-type semiconductor with a bandgap of ~3.6 eV. It is widely used in solar cells, displays, and sensors. Indium oxide based nanoparticles[278] and nanowires[279] were prepared. A rather simple method[280] of synthesis of In_2O_3 nanoparticles of controlled size (4, 6, or 8 nm) involves thermal decomposition of $In(acac)_3$ in oleylamine; the size of nanoparticles formed was controlled by varying the reaction conditions. In_2O_3 nanoparticles 30 nm in size can be produced by oxidation of metallic In nanoparticles.[281]

Coaxial nanotubes with the Ga_2O_3 inner layer inside and the ZnO outer layer were synthesized.[282]

Tin oxide SnO_2 is a stable wide-gap semiconductor ($\Delta E = 3.6$ eV). This is an excellent material for gas sensors, transistors, solar cells, and electrodes. SnO_2 nanoparticles were synthesized by hydrothermal,[283] sol-gel,[284] and CVD [285] methods, by magnetron sputtering,[286] and under microwave irradiation conditions.[287] A mesoporous material comprised of SnO_2 nanoparticles was prepared by high-temperature hydrolysis of mixed tin alcoholate/acetylacetonate.[288] Nanomaterials for gas sensors are synthesisized[289] using thermal decomposition of $[Sn(NMe_2)_2]_2$ in anisole at 150 °C; Sn/SnO_x nanoparticles thus formed are calcined in air at 600 °C and the resulting nearly 10-nm SnO_2 nanoparticles are doped with Pd and then transferred on a silicon nitride plate.

Single-crystalline SnO_2 is the best candidate for fabrication of miniature ultrasensitive gas sensors.[290] A one-step method of synthesis of SnO_2 nanorods ((8—15)×(150—200) nm) under mild conditions was developed.[291] Large amounts of SnO_2 nanostrips ((30—150)×(10—30) nm) hundreds of micrometers long[292] and 1-5-nm SnO_2 nanoparticles on the surface of BN nanotubes[293] were obtained.

Zinc oxide (ZnO) nanoparticles are usually synthesized by the reaction of zinc acetate with an alkali in isopropyl alcohol; nanoparticles thus obtained are stabilized by adding octanethiol to the solution.[200] A detailed study of non-hydrolytic route to ZnO nanoparticles 3.5 to 9.0 nm in size was reported.[294] It was shown[294] that a slow heating of the mixture of alkylamine, *tert*-butylphosphonic acid (TBPA), and zinc acetate is a simple and convenient method for the sysnthesis of ZnO nanoparticles from handy chemicals. Yet another method for the synthesis of rather large ZnO nanoparticles (~50 nm) is provided by thermal decomposition of zinc acetate in an oxygen flow.[295] In this case, the experimental setup allows thermogravimetric analysis and Raman spectra measurements to be done simultaneously and continuously during the thermal decomposition. Controlled oxidation of Et_2Zn with dioxygen in octylamine in the presence of TOPO produces more stable ZnO nanocrystals that are not prone to further enlargement.[296] A nanocomposite comprising 3.5-nm ZnO nanoparticles and poly(ethylene oxide) was obtained.[297] ZnO nanowires ($d = 20$—100 nm, $l =$ 0.5—10 μm) were synthesized by vaporization of zinc oxide powder,[298] vaporization of metallic Zn,[299] and from ZnO nanoparticles.[300] A more convenient route[301] to ZnO nanowires ($d = 80$—100 nm, $l \le 10$ μm) involves hydrothermal treatment of aqueous zinc carbonate. The zinc oxide nanowires are suitable for the synthesis of ZnO nanotubes.[302] Often, oxide nanoparticles are covered with shells of different compositions. Attempts at coating ZnO nanoparticles with an Al_2O_3 layer were reported;[303] however, analysis showed that the zinc oxide particles formed (50—60 nm in size) were covered with a $ZnAl_2O_4$ shell 4-5 nm thick.

Germanium oxide GeO_2 is a good insulator and a promising material for optical waveguides for integrated optics. GeO_2-based 1D structures (their synthesis was reported in Ref. 304) are also of interest because they combine stability and both insulating and catalytic properties.[305,306] Long α-GeO_2 nanowires ($d \approx 150$ nm, $l \approx 100$ μm) were obtained by thermal oxidation of nanocrystalline germanium.[307]

Titanium dioxide (titania) TiO_2 and titania-based materials are widely used in many fields owing to their biological and chemical inertness, high stability to photoinduced and chemical corrosion, and low cost. Titania is an efficient catalyst for the photooxidation and dehydrogenation of various organic compounds. However, TiO_2 has a bandgap of 3.2 eV and therefore efficiently operates on UV irradiation but not in the visible spectral region. At the same time, the TiO_2 and $TiO_{2-x}N_x$ nanoparticles 6 to 10 nm in size are efficient photocatalysts for photoinduced processes in the visible spectral region.[308]

The TiO_2 nanoparticles of various shape were synthesized[65] following the reaction

$$TiCl_4 + Ti(OR)_4 \rightarrow 2\,TiO_2 + 4\,RCl$$

in dioctyl ether in the presence of lauric acid and TOPO. Hydrolysis of TiF_6^{2-} in octadecylamine film permits the synthesis of 4-nm TiO_2 nanoparticles uniformly distributed over the matrix.[309] Preparation of films for hybrid solar cells from TiO_2 nanoparticles 50—300 nm insize was reported.[310] Multi-wall carbon nanotubes were also coated with the 2-10-nm TiO_2 nanoparticles.[311]

An original method for the growth of TiO_2 nanotubes on titanium foil was proposed.[312] Titanium foil was coated with a fraction of ultrasmall particles, which was separated by centrifugation of aqueous suspension of the commercially available TiO_2 powder, and treated with a NaOH solution in an autoclave at 160 °C; as a result, TiO_2 nanotubes (internal diameter 3.7 nm, outer diameter 12 nm) were grown on the foil surface (see also Ref. 313).

Zirconia (ZrO_2) nanoparticles were prepared by several methods,[31,314,315] but the best results were likely obtained by the reaction of zirconium isopropylate and zirconium chloride at 340 °C, which produced monodisperse 4-nm tetragonal ZrO_2 nanoparticles.[316]

5. Silicon, germanium, and silicon carbides

Research at the nanolevel is of particular interest for the investigations of narrow-gap semiconductors, because it allows the bandgap to be considerably increased. However, only a few studies on Si (ΔE = 1.17 eV) and Ge (ΔE = 0.67 eV) nanoparticles are available, while the "solution" routes to such particles are *rara avis*. The only study available so far[317] concerns an interesting method of synthesis of small (less than 3 nm) Si nanoparticles with simultaneous modification of the ligand shell. Namely, partial dechlorination of $SiCl_4$ by sodium in diglyme followed by treatment of the reaction mixture with H_2O, MeOH, or BuLi in order to produce Si nanoparticles with different surface properties. Such a change in the ligand shell affected not only the hydrophobic-hydrophilic characteristics but also (which is of crucial importance) permitted variation of the luminescence characteristics of nanoparticles. Most often, silicon nanoparticles were synthesized by laser vaporization and gas-phase evaporation of elemental silicon or in silane plasma.[318—320] Spherical Si nanoparticles ($d \approx 7$ nm) covered with a thin (~1 nm) layer of amorphous silica were prepared by arc evaporation of silicon.[321]

Low-pressure chemical vapor decomposition (LPCVD) of silane at 570—610 °C resulted in the formation of 2.5-3.0-nm-sized Si quantum dots on SiO_2 or Si_3N_4 substrates with a density of $6 \cdot 10^{11}$ cm^{-2}.[322] Silicon nanoparticles 4 nm in size were produced by CO_2 laser-induced decomposition of SiH_4 in a flow reactor.[323] Silicon nanowires were synthesized by CVD [324] and other method.[325,326] The surfaces of silicon nanowires treated with aqueous HF solution were shown to be hydrogen terminated and different Si—H bonds were detected.[327]

Germanium nanoparticles are often produced as incorporated into a SiO_2 matrix.[328,329] The sol-gel technique starting from traditionally used TEOS ($Si(OEt)_4$) and $GeCl_4$ was also reported for the first time.[330] In addition to TEOS, $HOOCC_2H_4GeCl_3$ was also used[331] as Ge source; this resulted in the formation of cubic Ge nanocrystals (6×9 nm) in the SiO_2 matrix. An interesting route to Ge quantum dots involves preparation of a thin layer of the $Si_xGe_yO_z$ mixed oxide on the substrate surface followed by selective reduction of the oxide upon subsequent fast (300 s) annealing at 1000 °C in N_2 atmosphere with the formation of a layer of 9.5-nm Ge nanoparticles on the SiO_2 surface with a density of $\sim 5 \cdot 10^{11}$ cm^{-2}.[332]

Regularities of the growth of Ge nanocrystallites on Si were considered in detail in a review.[333]

Germanium nanoparticles (d = 10—20 nm, l = 5 nm) precipitate on gold surface in the electrolysis of $GeBr_4$ in ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate.[334]

Germanium nanowires are of interest because the Borh exciton radius of Ge is larger than that of Si and, hence, germanium should be more responsive to the quantum size effects. Germanium nanowires were first prepared by the solvothermal method;[335] they were also grown on gold nanoparticles in supercritical cyclohexane.[336] More often, supercritical CO_2 was used[337] as solvent for the growth of ordered Ge nanowire structures with a density of $\sim 10^{12}$ cm^{-2}. But the simplest route to single-crystalline Ge nanowires is to use the CVD method with GeH_4 and gold nanoparticles as "catalysts".[338]

Silicon carbide SiC is a wide-gap semiconductor (ΔE = 2.2—2.8 eV). Exposure of the silicon carbide surface to high-power IR laser pulses leads to formation of SiC nanoparticles ~120 nm in size.[339] Silicon carbide nanowires (for methods of synthesis, see Refs 340 and 341) are of inerest because they can be used in electronic devices and composite materials. A simple and efficient method for the synthesis of large amounts of β-SiC nanowires (d = 40 nm, $l \le 500$ μm) involves their growth from the silicon plate in the reaction with methane and hydrogen at 1100 °C in the presence of Fe, Ga, or GaN nanoparticles as "catalysts".[342]

6. Conclusion

In this review we have clearly demonstrated the role of "chemical" synthetic methods for the formation of semiconductor nanoparticles with different compositions. A number of methods have been more thoroughly elaborated compared to the "classical" approaches (*e.g.*, synthesis of cadmium chalcogenide nanoparticles), while other methods require further development (synthesis of Si and Ge nanoparticles). But there is a marked trend, which can be formulated as follows: as the planar technology will approach its natural limit, the demands for "chemical" methods for the fabrication of various functional nanostructures will increase continuously.

Design of superstructures using chemically produced individual nanocrystalline quantum dots as "building blocks" and studies on the co-operative properties of these advanced artificial nanostructured materials has been a novel avenue of research.[343] Theoretical foundations of design of quantum computers using a system of interconnected quantum dots have been considered.[344] A trend toward the use of nanoparticles with different compositions for solving this problem is quite well-defined.

Unique possibilities of fabrication of quantum dots with various compositions and structures and with preset and very narrow size distributions in almost all pre-specified environments make the semiconductor nanoparticles an ideal object of 0D-physics.[345] Since inhomogeneity of the 0D or 1D nanomaterials leads to deterioration of many physical characteristics, successful development of nanotechnology requires reproducible fabrication of nanostructures with ordered arrangement of monodisperse nanoparticles of the same shape. All rational methods of solving this problem involve the use of "chemical" approaches.

For instance, a method of directed fabrication of 2D arrays of sub-10-nm single-crystalline Si nanorods with a density of $\sim 4 \cdot 10^{10}$ cm^{-2} using cobalt nanoparticle masks was developed by combining elements produced by the "classical" planar technology and materials based on chemically synthesized nanoparticles.[346] A rather large number of such "hybrid" approaches is available at the moment and they seem to play an increasing role.

Prospects for applications of semiconductor nanoparticles are quite versatile.[347] Recently, the possibilities of using quantum dots as emitters for thin-film light-emitting diodes (LED),[192] low-threshold lasers,[348] optical amplifiers for telecommunication networks,[349] biological labels,[239] light-emitting diodes,[100] photodetectors,[275] phosphors,[350] solar cells,[13] catalysts,[351] and photoelements[352] have been studied. Due to physical limitations and high cost, lithography methods can no longer be employed for further miniaturization of optical and electronic devices.[353] Therefore, intensive search for "nonlithographic" methods for fabrication of nanoscale integrated circuits (including the use of self-assembly of materials with complex nanoarchitecture from nanosized "building blocks" present in solution or at the interface) seems to be quite logical.[354—356] A single-electron transistor based on an isolated 5.5-nm CdSe nanoparticle placed in a ~10-nm gap between gold electrodes was fabricated and studied.[357] Nanofilaments in 1D nanostructures can act as both nanoelements and nanowires connecting them.

The first example of a solar cell element based on CdSe nanorods (7×60 nm) was reported.[13] The nanorods were dispersed in poly(trihexylthiophene) (a conducting polymer) and placed between electrodes in a conventional cell; the coefficient of solar energy conversion was 1.7%. Optical amplification in the system of 3D photonic crystals containing incorporated CdS nanoparticles was observed.[358] Quantum dots are suitable for design of electrochromic devices operating in the visible or IR spectral regions.[359]

The use of CdSe nanorods dispersed in liquid-crystalline media[360] seems to be quite promising for creation of new-generation displays. A technology was developed for fabrication of a nanocable ($d \approx 100$ nm) comprising a silicon substrate covered with a CdSe layer.[361] A core-shell nanowire with a GaN core (d = 5—40 nm, refractive index 2.54) and a $Al_{0.75}Ga_{0.25}N$ shell (thickness 50—200 nm, refractive index 2.25) was fabricated.[362] The authors[362] stated that they first realized an UV laser based on gallium nitride nanowires. Ultrahigh-density nanowire lattices with different compositions are thought[363] to be used for fabricaton of high-frequency nanomechanical resonators, high-density semiconductor sensors, *etc*.

Recently, the possibility of hydrogen storage in carbon nanotubes has been the subject of intensive studies. Likely, this is also a field of possible application of semiconductor nanotubes. For instance, ZnO nanowires can be used for hydrogen storage. The H_2 uptake is 0.83% w/w at room temperature and a pressure of 30 atm; about 71% of the stored hydrogen can be released under normal conditions.[364]

Undoubtedly, quantum dots are of considerable interest for nanobiotechnological and medical applications. In this connection, search for efficient methods for modification of the properties of quantum dots in order to attain biofunctionalization and biocompatibility is topical. Biocompatible fluorescent semiconductor quantum dots are developed and marketed by Quantum Dot Corp. (USA). The Evidot quantum-dot kits based on monodisperse CdSe nanocrystals are produced by and can be purchased from Evident Technologies, Inc. (USA).

From the aforesaid it follows that the time comes when nanoscale semiconductor particles possessing unique physical properties including the quantum size effects become components of various technological processes and devices. The design of such devices and development of corresponding technologies for production at economically acceptable level requires elaboration of efficient methods for fabrication of organized nanostructures from nanoscale semiconductor (and other) elements, which in turn gives an impetus to further improvement of promising "chemical" methods of synthesis, stabilization, and functionalization.

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