УДК: 544.77:546.48

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COLLOIDAL SOLUTIONS OF CdS/L-CYSTEIN NANOPARTICLES: FEATURES, SYNTHESIS AND PROPERTIES

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The article presents materials of the review of international and domestic scientific papers devoted to the technology of synthesis and research of properties of nanosized particles based on semiconductor material CdS, and particles of cadmium sulfide stabilized by biocompatible amino acid L-cysteine. The article mainly focuses on the results of research that reflect different methods of synthesis of nanoparticles of semiconductor materials, the main stages of their formation and maturation, the dependence of shape, size, morphology, and properties of particles on synthesis conditions, concentration, and the ratio of starting reagents in the reaction medium, the additive effect of components on studied properties of CdS / L-Cysteine nanoparticles.

The goal of the paper is to establish physicochemical regularities of processes of synthesis of low-dimensional CdS-based structures with the formation of colloidal solutions of CdS/L-Cys nanocrystals with predicted properties, elucidation of correlation between thermodynamic conditions of colloidal systems formation and morphology of nanoparticles, their size, and optical properties.

Keywords: semiconductor; nanosized particles; cadmium sulfide; optical properties; CdS/L-Cys.

Introduction

Cadmium sulfide CdS wideband semiconductor is one of the most studied materials in photo electronics. Reducing the size of CdS to 1–10 nm causes the bandgap to change from 2.4 eV (bulk material) to 4.5 eV. Starting from the size of nanocrystals (NCs) of 5-6 nm, there is a "blue shift" of the exciton CdS absorption band, which expands its application for photoelectric conversion in solar cells and photocatalysts, light-emitting and plane-panel diodes, as photoluminescent material in selective light filters, biolabels, etc.

The most available, reproducible, and productive method of synthesis of CdS NK is precipitation in liquid phase mediums in the presence of stabilizers. Purposeful control of NCs parameters and their reproduction require detailed information on optical characteristics of NCs, radiating and non-radiating recombination processes, influence on these parameters, as well as size and shape of nanocrystals of thermodynamic synthesis conditions, including nature and reagent content, temperature.

The analysis of the literature on the studies of synthesis conditions of CdS NC, stabilized by the biocompatible amino acid L-Cysteine (L-Cys), and the research of their properties showed that each author empirically chose a certain composition of the reaction system, which is why by the available data it is impossible to predict the properties of nanoparticles (NPs) and system stability as a function of composition in a wide range of concentrations of crystal-forming components of the solution. In addition, all the syntheses described in the literature were carried out under conditions of deaeration of the medium with the participation of inert gases, which in the mass use of such preparations is not profitable.

Features of nanosized semiconductors

Modern semiconductor electronics are developing by reducing the size of devices. However, for classical production methods, economic and technological aspects are getting more complicated when the size of the product

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DOI: 10.24144/2414-0260.2022.1.58-69

decreases slightly and economic costs increase exponentially. Nanotechnology is the next logical step in the development of electronics and other science-intensive productions.

Cadmium sulfide semiconductor (Eg = 2.4 eV, T = 298 K) and materials based on it remain at the top of the list of the most important materials of micro- and optoelectronics. Perhaps this is why cadmium sulfide was one of the first objects of study on a nanoscale and ultrafine scale [1-8].

Nanoobjects are classified according to their dimensions:

- *nanoparticles (NPs)* – a quasi-zero-dimensional object in which all the characteristic linear dimensions are values of the same order (not more than 100 nm);

- *quantum dots, or "artificial atoms" (quantum dots) (QD)* - semiconductor nanoparticles, the size of which is of the order of several (from 2 to 10) nanometers. By capturing electrons and localizing them in a small region, they are able to emit light with different wavelengths, depending on their size and energy levels. Energy levels can be controlled by changing the size, shape, and charge of a quantum dot;

- *nanorods, nanowires, nanofibers, nanotubes* - quasi-one-dimensional objects in which one size is an order of magnitude larger than the other two in the nanoscale;

- *nanodisks* - quasi-two-dimensional objects in which two dimensions exceed the third, which is in the nanoscale;

- *ultra dispersed particles (UDP)* - powders with a size of 0.5 μm and above.

The uniqueness of the physicochemical properties of NPs of semiconductors is due to three main reasons:

1) their size is commensurate with the Bohr radius of excitons in semiconductors, which determines the optical, luminescent, and redox properties of NPs;

2) the proportion of "surface" atoms for which the coordination number, symmetry of the local environment, etc., are different than for "bulk" atoms, is a significant part of the total number of atoms of NP.

Thus, in a 5 nm CdS nanocrystal, about 15% of the atoms are located on its surface. "Surface" atoms make a great contribution to the thermodynamic characteristics of solid bodies and for nanoparticles mainly determine the structural transitions and melting point;

3) the intrinsic size of nanoparticles is commensurate with the size of molecules, which determines the specifics of the kinetics of chemical processes on their surface.

As the size of the NC decreases, the width of the electronic and hole zones decreases, which leads to an increase in the total energy of the optical transitions. This is one of the main manifestations of quantum-sized effects - the so-called "blue shift" of the edge of the absorption band and the peak of photoluminescence (PL) in the short-wavelength region with decreasing particle size. The "blue shift" of the exciton absorption band for CdS is observed starting from the crystal size of 5–6 nm [1, 3]. By varying the size of the NC from 30 to 1 nm, it is possible to vary the width of the bandgap of CdS from 2.4 eV (bulk material) to 3 eV in fact within the entire optical spectrum [6] (Fig. 1).

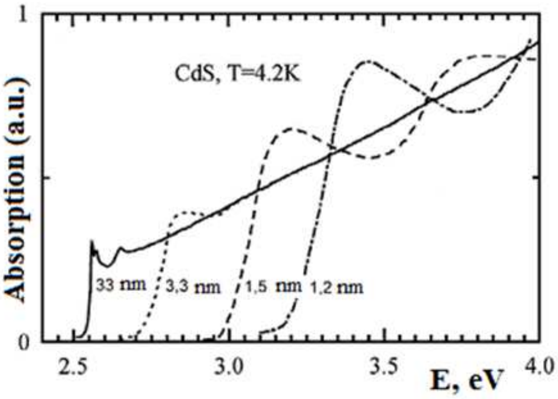

Fig. 1. The absorption spectrum of colloidal solutions of CdS nanoparticles of different radii [6].

The variety of possibilities for the use of semiconductor nanoparticles has formed certain requirements for their quality:

- fixed size;
- narrow distribution by size;
- photostability;
- high quantum yield of luminescence emission, etc.

Such properties make NPs ideal fluorescent biomarkers in analysis based on biospecific ligand-receptor interactions in various in vivo and in vitro bioanalytical systems in which the use of traditional organic fluorophores is limited by insufficient photostability [9, 10].

Quantum-dimensional effects of semiconductor nanoparticles

The literature distinguishes between dimensional effects, the appearance of which is associated with an increase in the specific surface area and the degree of defective with decreasing crystal size, as well as the effects caused by a radical change in the electronic structure of the semiconductor. The difference between such effects is also in the dimensional range of their manifestation. Nanoparticles that exhibit quantum-dimensional effects are called quantum-dimensional particles or quantum dots, emphasizing their special electronic structure. From the point of view of the photonics of semiconductor nanoparticles, the most important are the quantum-dimensional effects associated with changes in the electronic structure. Basically, these changes lead to the expansion of the band gap of the semiconductor and reduction of the density of electronic states along the edges of the conduction band and valence band [6, 11-13].

The absorption of light by semiconductor NPs with nondegenerate energy zones depends on two factors - the size of the gap between the allowed zones and the density of defective levels in the forbidden zone. The first factor determines the position of the long-wavelength edge of the absorption band (λtr), and the second - the shape of the absorption band near its edge and the absorption intensity in the region hυ < Eg (where hυ is the energy of the light quantum). The absorption of light by nanoparticles, depending on the energy of the light quantum, can lead to direct and indirect interband electronic transitions. For a direct zone-to-zone transition, the absorption bands are characterized by a distinct edge under the condition that hυ = Eg and a slight absorption under the condition that hυ < Eg (Fig. 2a). Absorption bands, which correspond to indirect zone-to-zone transitions, do not have a distinct absorption edge and have a sloping appearance (Fig. 2b).

Nanocrystals, the size of which corresponds to the region of strong quantum constraint, are in the transition range, in which there is a gradual destruction of the band structure of semiconductor and the emergence of a set of discrete electronic levels characteristic for substances with molecular dispersion. Such nanoparticles are often called nanoclusters.

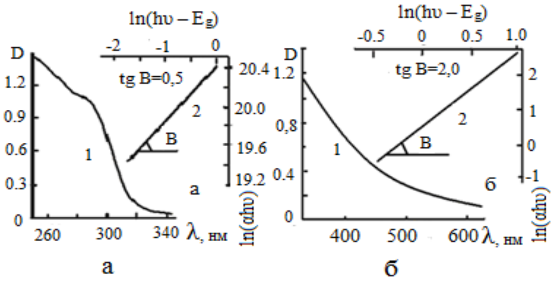

Fig. 2. a – the spectrum of optical absorption of semiconductor corresponding to direct zone-zone transitions (1) and anamorphosis in coordinates ln(αhυ) - ln(hυ - Eg) (2);
b – the spectrum of optical absorption of semiconductor corresponding to indirect transitions (1) and anamorphosis in coordinates ln(αhυ) - ln(hυ - Eg) (2) [14].

The increase in the band gap due to the quantum constraint effects is manifested in the absorption spectra of semiconductor NPs in the form of a hypsochromic shift of the long-wavelength edge of the fundamental absorption band. The smaller the particle size, the larger the absorption bands. The hypsochromic shift of the edge of the absorption band (or the increase in the band gap energy ΔE) is inherent in all semiconductor crystals that are in the quantum constraint mode.

Luminescence of semiconductor nanocrystals

An important tool for studying electronic processes in semiconductors is to measure the ability of photoluminescence. The latter occurs when electrons are excited by absorbing light but radiating its already different spectral composition. Photoluminescence (PL) - is radiation that is surplus over thermal radiation that lasts for a period significantly longer than the period of light oscillations.

After the relaxation of "hot" charge carriers to the bottom of the respective energy zones, there are 4 possible ways of consuming their energy: 1) relaxation without radiation into the ground state; 2) capture of the charge by surface traps; 3) recombination radiation; 4) interphase transfer to absorbed substrates.

Recombination radiation in semiconductor NPs can occur in two ways. The first method is band-band recombination of photogenerated charges, which is also called exciton luminescence. The position of the maximum of the exciton luminescence band coincides with the edge of the absorption band, and the energy becomes Eg. In semiconductors characterized by direct band-band electronic transitions, exciton luminescence is observed in the nanosecond time range and is characterized by quantum yields from 10-3 to 10-1 depending on the nature and method of obtaining nanoparticles. In the case of semiconductors with indirect transitions, exciton luminescence occurs in micro- and milliseconds with very low quantum yield.

The second type of luminescence occurs as a result of the recombination of valence band holes with electrons captured in the process of thermal trapping by surface traps, or electrons and holes that move under the action of thermal motion in small traps (defective or donor-acceptor luminescence). The energy levels of traps are in the forbidden zone of semiconductor, and their location is determined depending on the nature of the defects and their local environment. That is why the bands of donor-acceptor luminescence are wide and shifted relative to the bands of exciton luminescence in the long-wavelength region. The appearance of bands of donor-acceptor luminescence in the emission spectra at room temperature is a characteristic feature of semiconductor crystals that have a developed and structurally imperfect surface.

According to Stokes' law, photoluminescence is characterized by a longer wavelength (lower photon energy) compared to exciting light. The difference in the energies of the excitatory and emitted photons is called the Stokes loss, and the difference in the wavelengths corresponding to the maxima in the absorption and PL spectra is called the Stokes shift. In systems with colloidal solutions of semiconductors, the Stokes shift is usually explained by the distribution of NPs in size. In this case, the position of the maximum of the PL band is formed mainly by the radiation of the NPs of the largest size in the distribution. Another explanation for the Stokes shift is the local states on the NPs surface. They can be formed due to poor passivation of broken bonds of external atoms [15-17].

Methods of synthesis of CdS nanoparticles

Extensive opportunities for the practical application of nanosized CdS led to an intensive increase in the number of publications describing various methods of its synthesis. In the 1990s, a universal method for producing cadmium chalcogenide nanocrystals CdE (E = S, Se, Te) using organometallic compounds was proposed [2], but the ecological unattractiveness of the latter stimulated the development of other chemical synthesis methods.

The so-called "wet" (in liquid phase) methods of synthesis of CdS NPs can be divided into the following main groups: synthesis of CdS NPs in aqueous or organic solutions of the corresponding salts by controlled addition of anions (cations) or hydrolysis [17-33]; in aerosols (reverse micelles) [34-38]; Langmuir-Blodget films [39, 40]. Recently, CdS NPs have also been synthesized in polymers [41-43]; glass [44]; zeolites [45].

The most common are "wet" synthesis methods that do not require special equipment and can be implemented in both laboratory and industrial conditions. Cadmium sulfide nanoparticles are usually synthesized by the reaction of a water-soluble metal salt (halide, nitrate, perchlorate, acetate, formate, stearate, etc.) or cadmium oxide and a sulfide-containing compound in the presence of a suitable stabilizer [46]. Hydrogen sulfide, sodium sulfide and thiosulfate, thioacetamide, thiourea, and even L-cysteine are used as a source of sulfide ion [1, 2, 8, 24, 35, 47]. In almost all works the deaeration stage is carried out to eliminate the possibility of oxidation of sulfide ions. Syntheses are also performed in organic polar protonic (ethanol, ethylene glycol, diethylene glycol, glycerol, mono- and diethanolamine, methanol) and polar aprotic solvents (dimethylformamide, dimethyl sulfoxide) [18, 21, 24, 25, 29, 34, 36, 48].

Synthesis and properties of CdS nanoparticles in colloidal solutions

Despite the fact that the essence of the chemical process of binary compound formation is extremely simple - the interaction of cation and anion, quite a lot of papers are devoted to the study of methods for the synthesis of CdS NPs today.

The simplest and most common way to obtain CdS nanoparticles is the synthesis of starting reagents in solution by interrupting the reaction at a certain point in time by introducing a stabilizer [17-33]. According to [8, 49], the formation of such NPs occurs in the following stages: 1) the rapid process of nucleation in the formation of the reaction mixture; 2) the growth of the NPs due to the influx of ions from the solution; 3) Oswald maturation; 4) saturation of the solution with nanoparticles. The ratio of the speeds of these stages is shown in Fig. 3.

The increase in the size of NPs due to the dissolution of small particles (Oswald's maturation mechanism) is due to the fact that smaller particles are thermodynamically less stable due to their greater surface free energy.

Unfortunately, almost all colloidal solutions of NPs have a low resistance to coagulation and large size dispersion. Coagulation can be avoided by passivating the surface of nanoparticles with hydroxyl ions [50, 51], thiourea, amines or ammonium [52, 53], starch [54]. Another way to stabilize colloidal solutions of NPs is to coat their surface with sodium polyphosphate $(NaPO_3)_n$ [22], thiols [55-57], or gelatin [58]. The growth of CdS nanoparticles during the reaction can also be interrupted by a sudden increase in the pH of the solution [59, 60].

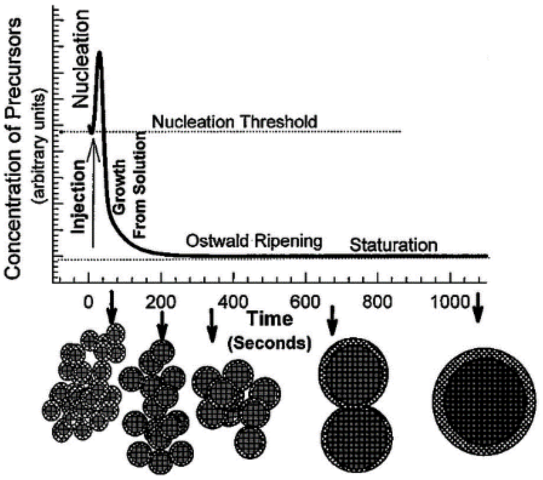

Fig. 3. Stages of nucleation and growth of nano-particles: injection; nucleation; growth of NPs from the solution; Oswald's maturation; saturation [8].

In this way, a stable colloidal solution can be obtained, powdered NPs isolated from it, and then the colloidal solution can be obtained again by dissolving the powder in a solvent.

The emergence of quantum-dimensional effects in the CdS NPs, accompanied by a shift of the edge of the absorption band in the short-wavelength region, begins when the particle size is less than 10 nm. The amount of displacement depends on the nature and amount of stabilizer and formed nanoparticles. For nanoparticles stabilized with polyvinyl alcohol, the offset is 15-20 nm, and the use of gelatin as a stabilizer results in an offset of 60 nm or more [54].

CdS NPs structure

A major problem for nanosized particles is determining the type of crystal lattice of small NPs up to 10 nm. Like macro crystals, nanosized CdS can be formed with a cubic (sphalerite) or hexagonal (wurtzite) structure. According to the literature, the type of CdS NPs crystal lattice is determined by various factors: nature and concentration of precursors, nature of the medium (solvent), temperature and duration of synthesis, external influences (irradiation, radiation treatment), etc. [19, 28, 60-63].

The dependence of the shape of nanocrystals on the concentration of precursors is illustrated in Fig. 4. The initial crystalline form of the embryo with a certain "magic number" (magic-sized nuclei) of structural units may remain conditionally as a point (dot) at low monomer content, change to rice-shape at medium or become rod-shaped (rod) or tetrahedral (multipod) with high and ultra-high content of source components [63].

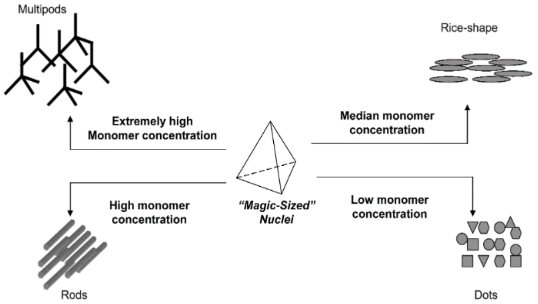

Fig. 4. The effect of monomer concentration on the form of CdS NPs [63].

The results of computer analysis obtained in [64, 65] led to the conclusion that small (Ø <5 nm) CdS nanoparticles are characterized by a special disordered structure, different from the crystal structure of wurtzite and sphalerite, characteristic of bulk crystals of this semiconductor. In [66], based on theoretical calculations and X-ray spectroscopy and electron microscopy studies, it was concluded that the cubic lattice has less energy than the hexagonal lattice, and therefore is more stable. The stability of both phases is determined by the size of the NPs and the environment, so depending on the conditions of obtaining, the shape of NPs can be different (spherical, rods, tetrapods, fungal, tubular, flakes, "hedgehogs", etc.).

In [32] it was shown that the size and morphology of nanoparticles are influenced by both the concentration of precursors and the environment of the nanocrystal nucleus, i.e. the nature of "counterions" or the ionic strength of the solution. Only by replacing the anion in the starting salt of Cadmium, while maintaining other synthesis conditions, it is possible to change the size of NPs by an order of magnitude and obtain particles of different shapes. [70]. One of the reasons for such a variety of forms of nanosized particles is the kinetics of their growth, which, in turn, is determined by the parameters of the processes of complexation and "release" of the cation.

Nanoparticles of larger fixed sizes are synthesized by attaching additional molecules to the original cluster of small size, stabilized in colloidal solutions by organic ligands [67]. Thus, in [68] it was found that the size of CdS clusters coated with thiophenolate ions can be increased by adding additional metal sulfide to the solution. Such polymerization of inorganic compounds can be used to obtain large clusters of semiconductors of fixed size based on small particles.

A number of studies have shown that NPs often have distinct faces and their shape is similar to the shape of macroscopic crystals [6]. In [69], based on clusters $[Cd_{10}S_4(SC_6H_5)_{16}]^{4-}$ of pyramidal shape consisting of 30 cadmium and sulfur atoms, clusters $[Cd_{20}S_{13}(SC_6H_5)_{22}]^{8-}$ which consist of 55 atoms of cadmium and sulfur were obtained. The addition of five additional sulfur ions results in the joining of two small clusters into one large cluster. The formation of a large cluster of two small ones can be illustrated by a diagram (Fig. 5).

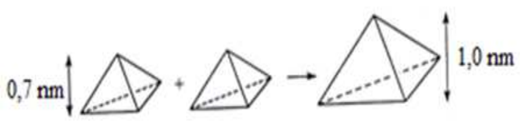

Fig. 5. The scheme of formation of a large cluster of two small [69].

The pyramidal structure of clusters $[Cd_{20}S_{13}(SC_6H_5)_{22}]^{8-}$ confirmed by X-ray diffraction analysis. Subsequent addition of sulfide ions yields a tetrahedral cluster $Cd_{32}S_{14}(SC_6H_5)$ 36 containing 82 cadmium and sulfur atoms [68].

Synthesis and properties of CdS nanoparticles stabilized by L-Cysteine

Extensive possibilities of controlling the size and, consequently, the properties of CdS NPs when using a biocompatible L-cysteine stabilizer in biology and medicine (as biolabels) stimulated the search for optimal methods for their production [20, 32, 47, 48, 55-57, 68-72].

L-cysteine (Cys) - is one of the twenty amino acids that are part of proteins, which plays an important role in the formation of the secondary structure of proteins due to the formation of disulfide bridges. Its structural formula is shown in Fig. 6. It is a sulfur-containing hydrophilic acid, well soluble in water. The stabilizing effect of cysteine is due to the presence of thiogroups in its molecules and its ability to form covalent bonds with CdS nanocrystal.

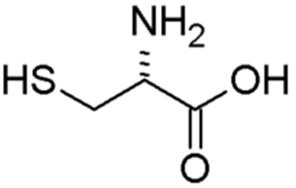

Fig. 6. Graphic formula of L-cysteine.

Depending on the acidity of the environment, cysteine can carry a positive or negative charge. The ability of cysteine molecules to change charge depending on the pH of the environment can be used to obtain nanocrystals with both positively and negatively charged surfaces. This opens up greater possibilities for the use of such materials compared to NPs, which can have only a certain positive (e.g., stabilized aminoethaniol) or negative (e.g., stabilized thioglycolic acid) charge.

For example, in a work [77], the authors make an assumption about the structure of CdS/L-Cysteine nanoparticles Fig. 7, which correlates with information in other works [78, 10].

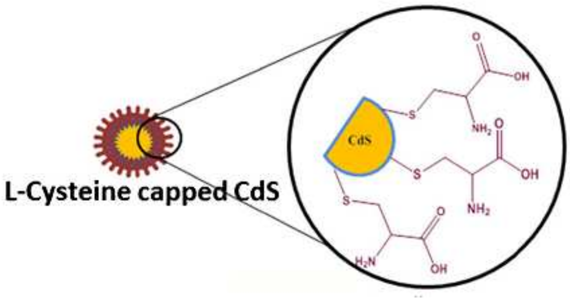

Fig. 7. Structure of CdS/L-Cysteine nanoparticles [77].

The technology of open fluorescent samples is a new way to visualize cell structure and study cellular processes. Organic fluorophores such as rhodamine and fluorescein isothiocyanate are most often used for this purpose. However, these organic dyes have disadvantages due to their low photostability, narrow absorption zones, and wide spectrum of radiation. Therefore, semiconductor nanoparticles are considered promising for application in this field. Quantum dots used as biolabels have two requirements: water solubility and biocompatibility.

By examining incubated cells with L-cysteine-stabilized CdS nanoparticles, it is possible to obtain information about the cell shape, average concentration of quantum dots introduced into the cell, their intracellular distribution, and luminescence attenuation time [9, 10, 12, 71, 78]. It is confirmed that these quantum dots are more resistant to radiation than chlorophyll.

In a review paper by Gaucher with co-authors [72], the possibilities are shown of using luminescent CdS/L-Cysteine NPs in clinical diagnosis to identify various components of biological media - mannitol, urea, uric acid, glucose, sorbitol or sucrose, amino acids.

L-cysteine-stabilized CdS NPs are also widely used in analytical chemistry (particularly as sensors of cations of d-elements - Zn^{2+}, Ag^{+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Hg^{2+} and s-elements Ca^{2+}, Mg^{2+} [12, 72-76]), as photocatalysts [3, 17, 23, 77]) as active elements of light-emitting diodes [30, 31].

Analysis of literature data indicates the number of technological factors that determine the optical properties and shape of the synthesized NPs, covered with a stabilizer of the same nature. Sometimes this leads to ambiguity of results and contradictory conclusions in the works of different authors. At the same time, the problem of generalizing literature recommendations with the possibility of predicting the properties of a system with a wide range of component concentrations remains difficult. Until recently, only in the work of Barglik-Chori and others. [69] an attempt was made to take a systematic approach to the study of correlations "composition - properties". The results of these authors on the dependence of the bandgap of CdS nanoparticles on the concentration of L-cysteine and sulfur-containing compound HMDST (bis-trimethylsilyl sulfide) under the condition $[L\text{-}Cys]/[Cd^{2+}] = 3$, $[HMDST]/[Cd^{2+}] = 1$, pH = 4 and 8 are generalized using method of statistical design of the experiment.

The method of statistical design of the experiment is based on the use of polynomial regression:

$$Y = \sum_{i=1}^{N} b_i x_i + \sum_{i=1}^{N} b_i x_i^2 + \sum_{i,j=1}^{N} b_i x_i x_j \qquad (1),$$

where $x_{i,j}$ are independent variables (concentrations of precursors *i* and *j*, *b* - are coefficients in the regression equation.

The results of determining [69] the concentration dependence of the bandgap of CdS/L-Cys nanoparticles are visualized in Fig. 8.

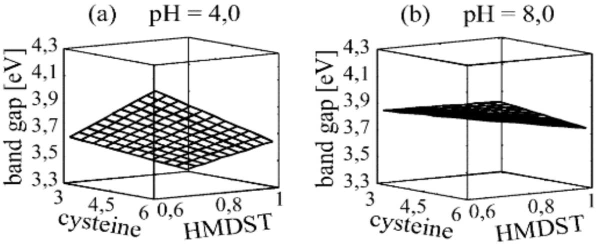

Fig. 8. The bandgap of CdS/L-Cys NPs, determined according to the absorption spectra data, as a function of the concentration of the stabilizer (3.0 - 6.0 mol. Cysteine) and sulfiding agent HMDST (0.6 —1.0 mol.) for (a) pH = 4 and (b) pH = 8; $[L\text{-}Cys]/[Cd^{2+}] = 3$ [69].

Conclusions

On the basis of the conducted literary research the following conclusions are made:

1. Literature data on the studies of the additive effect of the components of the system Cd^{2+} - L-Cysteine - S^{2-} on the properties of colloidal

solutions of CdS/L-Cysteine NPs are little studied and are mostly partial, unsystematic.

2. There are no data in the literature on the synthesis of colloidal solutions of CdS NPs stabilized by L-Cysteine in a potentially oxidizing environment (without creating an inert environment).

3. The properties of colloidal solutions of CdS/L-Cysteine NPs depending on the synthesis temperature and the value of the hydrogen index of the system are little studied.

4. The influence of synthesis conditions and system composition on the kinetics of CdS/L-Cysteine NPs maturation has practically not been researched.

5. The search for opportunities for a comprehensive analysis of the impact of various technological factors on the characteristics of NPs and their design remains relevant.

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The article was received by the editors on: 16.05.2022.

КОЛОЇДНІ РОЗЧИНИ НАНОЧАСТИНОК CdS/L-ЦИСТЕЇН: ОСОБЛИВОСТІ, СИНТЕЗ ТА ВЛАСТИВОСТІ

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В статті представлено матеріали огляду міжнародних та вітчизняних наукових робіт присвячених технології синтезу та дослідженню властивостей нанорозмірних частинок на основі напівпровідникового матеріалу CdS, та частинок кадмій сульфіду стабілізованого біосумісною амінокислотою L-цистеїн. Основну увагу у статті приділено результатам досліджень, що відображають різні методики синтезу наночастинок напівпровідникових матеріалів, основні стадії їх формування та дозрівання, залежність форми, розміру, морфології та властивостей отримуваних частинок від умов синтезу, концентрації та співвідношення вихідних реагентів у реакційному середовищі, адитивного впливу компонентів системи на досліджувані властивості наночастинок CdS/L-Цистеїн.

Метою роботи є встановлення фізико-хімічних закономірностей процесів синтезу низькорозмірних структур на основі наночастинок CdS з утворенням колоїдних розчинів нанокристалів CdS/L-Cys із прогнозованими властивостями, з’ясування кореляції між термодинамічними умовами утворення колоїдних систем та морфологією наночастинок, їх розміром і оптичними властивостями.

Ключові слова: напівпровідник; нанорозмірні частинки; кадмій сульфід; оптичні властивості; CdS/L-Cys.