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## Research of CdS/L-cystein colloid solutions using the method of mathematical planning

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In the work, the additive effect of the content of crystal-forming ions  $\text{Cd}^{2+}$  and  $\text{S}^{2-}$  and the stabilizer L-Cys using the method of mathematical planning of the experiment on the process of formation of CdS/L-Cys nanoparticles in potentially oxidizing conditions (without deaeration of precursor solutions) and the optical properties of colloidal solutions were investigated. obtained under conditions of  $\text{pH} = 7$  and temperature of  $22^{\circ}\text{C}$ . By statistical processing of the results, equations were obtained and diagrams of concentration dependences of the wavelength of the optical absorption edge of colloidal solutions of CdS semiconductor nanoparticles in the  $\text{Cd}^{2+} - \text{L-Cys} - \text{S}^{2-}$  system were constructed.

**Keywords:** nanoparticles (NPs), mathematical planning, optical properties, dependence diagrams, concentration region.

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### Introduction

The unique properties of semiconductor material based on nanosized particles, in particular CdS, have a wide range of applications in photo and optoelectronics, photocatalysis, analytical chemistry, as detectors in medical diagnostics and food technology, telecommunication technologies, etc. [1-7].

The spheres of application of such particles depend on the chemical and physical properties that the synthesized objects will exhibit. That is why it is extremely important to choose the synthesis conditions (ratio of components, concentrations of starting solutions, pH of the synthesis medium, nature of the stabilizer, temperature, pressure, presence or absence of an oxidizing medium, interfering ions, etc.) in such a way as to obtain nanoparticles with specified properties.

### I. Experimental

In order to optimize and save the use of reagents, time and work of the experimenter, as well as the maximum result of the research with the performance of the

minimum number of experiments, the method of mathematical planning of the experiment - the method of simplex Scheffe lattices [8, 9] and the Statistica program is used in the work.

The synthesis of CdS nanoparticles was carried out by a chemical method from solutions of the corresponding salts according to the precipitation reaction:



For the experiments, high-quality starting reagents were used: 0.5 M solution of  $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$  "high quality"; 0.05M solution of L-Cysteine ( $\text{HOOC-CH}(\text{NH}_2)\text{-CH}_2\text{-SH}$ ) "h.c."; 0.5 M solution of  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  (99% purity Aldrich), 0.1 M solution of NaOH. The synthesis was carried out in an oxidizing environment (without prior deaeration of the starting solutions). Colloidal solutions of CdS NPs stabilized by the amino acid L-cysteine were obtained in a volume of 100 ml with variable concentrations of CdS nanoparticles from  $2 \cdot 10^{-3}$  to  $7 \cdot 10^{-3}$  mol/l, molar ratio  $[\text{Cd}^{2+}]/[\text{S}^{2-}]$  from 0.47 to 2.11. The concentration of the stabilizer in the system ranged from 30.0 to 80.0% of the total composition of the system.

A fixed volume of 0.05 M thiol-stabilizer solution was

added to a volume of 0.5 M CdCl<sub>2</sub>·2.5H<sub>2</sub>O solution fixed with an accuracy of 0.01 ml. Immediately after adding L-Cysteine, the solution acquires a white color due to the formation of a complex between L-Cysteine and cadmium ions. After draining these solutions, the pH of the mixture is set at the level of 3–3.5. Synthesis at such a hydrogen rate leads to the formation of a coarse crystalline precipitate of cadmium sulfide. Therefore, to establish the appropriate pH of the solution, before adding sulfide ions, NaOH solution was introduced with vigorous stirring. The pH of the solution was determined using a pH-meter of the brand pH-301.

A series of syntheses of CdS/L-Cys nanoparticles was carried out at a fixed initial pH value of the medium equal to 7. After setting the appropriate pH, a fixed volume of 0.5 M Na<sub>2</sub>S solution was added to the solution with intensive stirring. The formation of cadmium sulfide particles was observed visually by the appearance of the color of the solution from light lemon to yellow, which was stirred for another 15 min using a magnetic stirrer at a speed of 100 rpm and by optical absorption spectra.

In order to generalize the results of the study of the effect of changing the concentration of precursors on the sizes of NPs and the optical properties of their colloidal solutions, the composition of the reaction system was chosen based on the simplex-lattice plan according to the Scheffé method. The composition of 15 points, determined according to the Scheffe simplex lattice plan, expressed in molar ratios and, according to each composition, in percentages within the limits of the concentration of precursors in the studied area, is given in Table 1. (the studied area is bounded by the equilateral triangle A<sub>4</sub>B<sub>4</sub>C).

Based on previous studies, concentration areas were established, within which color precipitates were observed immediately after pouring solutions or within four days.

Therefore, in the work, research is conducted in the field of stable colloidal solutions for more than 4 days.

The formation of CdS NPs in each of the 15 studied solutions is proven by the presence of a characteristic clear maximum in the absorption spectra in the wavelength range from 390 to 430 nm, which corresponds to a blue shift in relation to single-crystal (bulk) CdS ( $\lambda_{lim} = 515$  nm).

The size of the synthesized nanoparticles was calculated according to the known formula:

$$R = h(8\mu\Delta E_g)^{-1/2}, \quad (2)$$

where R – maximum particle radius CdS (nm),  $\mu = [(m_e^*)^{-1} + (m_h^*)^{-1}]^{-1}$ , h-Planck's constant ( $h = 4.135 \cdot 10^{-15} \text{ eV} \cdot \text{s}$ ),  $m_e^* = 0.21 m_e$ ,  $m_h^* = 0.8 m_e$  - effective masses of electrons and holes in CdS,  $m_e$  - rest mass of an electron ( $m_e = 9.1093 \cdot (16) \times 10^{-31} \text{ kg}$ ),  $\Delta E_g$  - the gap value difference (2.4 eV).

## II. Results and Discussion

According to estimates by the formula, the size of the particles (diameter 2R) varies from 3.7 to 8.0 nm (Table 2), which corresponds to the nanoscale.

With a small deviation from the equimolar ratio of Cadmium and Sulfur ions, an increase in the stabilizer content naturally limits the growth of nanoparticles, the size of which does not exceed 10 nm in general.

Since all solutions are homogeneous in the area of the studied compositions, according to the data in Table 1, an equation was derived that describes the dependence of the absorption edge  $\lambda_{lim}$  on the composition of the three-component system (Cd<sup>2+</sup> - L-Cys - S<sup>2-</sup>) with the approximation of the third degree (STATISTICA

**Table 1.**

The composition of solutions corresponding to 15 points of the simplex-lattice Scheffe plan for the studied area of the defined triangle A<sub>4</sub>B<sub>4</sub>C

№ points	№ according to Scheffe's plan	Ratio in moles per 50 ml, ( $\cdot 10^4$ ), mol			Composition in %			Encoded scale		
		Cd <sup>2+</sup> A <sub>4</sub>	L-Cys C	S <sup>2-</sup> B <sub>4</sub>	Cd <sup>2+</sup> A <sub>4</sub>	L-Cys C	S <sup>2-</sup> B <sub>4</sub>	Cd <sup>2+</sup> A <sub>4</sub>	L-Cys C	S <sup>2-</sup> B <sub>4</sub>
1	x <sub>2</sub>	4.75	3.00	2.25	47.50	30.00	22.50	1.00	0	0
2	x <sub>1222</sub>	3.81	4.25	1.94	38.12	42.50	19.37	0.75	0.25	0
3	x <sub>12</sub>	2.87	5.50	1.62	28.75	55.00	16.25	0.50	0.50	0
4	x <sub>1112</sub>	1.94	6.75	1.31	19.37	67.50	13.12	0.25	0.75	0
5	x <sub>1</sub>	1.00	8.00	1.00	10.00	80.00	10.00	0	1.00	0
6	x <sub>1113</sub>	1.31	6.75	1.94	13.12	67.50	19.37	0	0.75	0.25
7	x <sub>13</sub>	1.62	5.50	2.87	16.25	55.00	28.75	0	0.50	0.50
8	x <sub>1333</sub>	1.94	4.25	3.81	19.37	42.50	38.12	0	0.25	0.75
9	x <sub>3</sub>	2.25	3.00	4.75	22.50	30.00	47.50	0	0	1.00
10	x <sub>2333</sub>	2.87	3.00	4.12	28.75	30.00	41.25	0.25	0	0.75
11	x <sub>23</sub>	3.50	3.00	3.50	35.00	30.00	35.00	0.50	0	0.50
12	x <sub>2223</sub>	4.12	3.00	2.87	41.25	30.00	28.75	0.75	0	0.25
13	x <sub>1223</sub>	3.18	4.25	2.56	31.87	42.50	25.62	0.50	0.25	0.25
14	x <sub>1123</sub>	2.25	5.50	2.25	22.50	55.00	22.50	0.25	0.50	0.25
15	x <sub>1233</sub>	2.56	4.25	3.18	25.62	42.50	31.87	0.25	0.25	0.50

program):

$$\lambda_{lim} = 415x_1 + 494x_2 + 486x_3 - 172x_1x_2 + 36x_1x_3 - 140x_2x_3 - 205x_1x_2(x_1 - x_2) - 160x_1x_3(x_1 - x_3) - 75x_2x_3(x_2 - x_3) - 153x_1x_2x_3 \quad (3)$$

and fourth degree (Scheffé method):

$$\lambda_{lim} = 417x_1 + 489x_2 + 483x_3 - 192x_1x_2 + 12x_1x_3 - 172x_2x_3 + 43x_1x_2(x_1 - x_2) + 43x_1x_3(x_1 - x_3) - 48x_2x_3(x_2 - x_3) + 85(x_1 - x_2)^2x_1x_2 + 112(x_1 - x_3)^2x_1x_3 + 538(x_2 - x_3)^2x_2x_3 + 2677x_1^2x_2x_3 - 2229x_1x_2^2x_3 + 144x_1x_2x_3^2 \quad (4)$$

in which the coefficients near the first terms of the equations ( $x_1, x_2, x_3$ ) agree satisfactorily.

The design of these equations is illustrated by diagrams of the dependence of the absorption edge on the composition of the solution - fig. 1 and 2.

From the projections (Figs. 1 and 2) it can be seen that

by an equimolar ratio ( $[Cd^{2+}]/[S^{2-}]=1$ ) the absorption edge is mainly determined by the content of the stabilizer: with an increase in the content, the value of  $\lambda_{lim.}$ , and the size of NPs decreases.

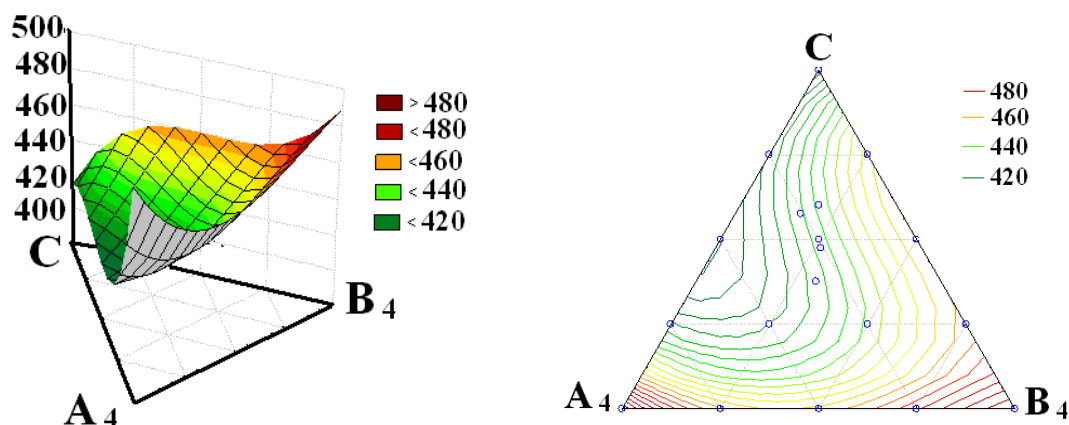
In cysteine-depleted solutions, an excess of both crystal-forming ions stimulates an increase in the size of

**Table 2.**

Dependence of optical characteristics of colloidal solutions of CdS/L-Cys NPs from the composition of the system

N π/π	$\lambda_{lim}, nm$	$\lambda_{max}, nm$	2R, nm (1)	$E_g, nm$	$\lambda_{max.lum.}, nm$	Stokeslandslide, eV
1	489	398	8.0	2.5	486	0.57
2	435	393	4.5	2.8	480	0.57
3	405	386	3.7	3.1	488	0.67
4	407	388	3.7	3.0	516	0.79
5	417	395	3.9	3.0	516	0.73
6	445	416	4.8	2.8	**	*
7	453	415	5.5	2.7	490	0.45
8	470	429	6.1	2.6	490	0.36
9	483	426	7.3	2.6	**	**
10	482	433	7.3	2.6	523	0.49
11	443	408	4.7	2.8	481	0.46
12	476	428	5.7	2.6	**	**
13	414	389	3.8	3.0	519	0.80
14	448	413	3.8	2.8	496	0.50
15	447	415	4.9	2.8	486	0.44

Note: \*\* - measurements were not performed;  $\lambda_{lim}$  - optical absorption edge,  $\lambda_{max}$  - optical absorption maximum, 2R - particle size (calculated according to formula 2),  $E_g$  - band gap width,  $\lambda_{max.lum.}$  - luminescence maximum.



**Fig. 1.** 3D graph (by a polynomial of the 3rd degree) of the dependence of the absorption edge of CdS/L-Cys colloidal solutions from the studied area  $A_4B_4C$  on the content of the components of the  $Cd^{2+} - L-Cys - S^{2-}$  system (left) and its projection on the plane (right).

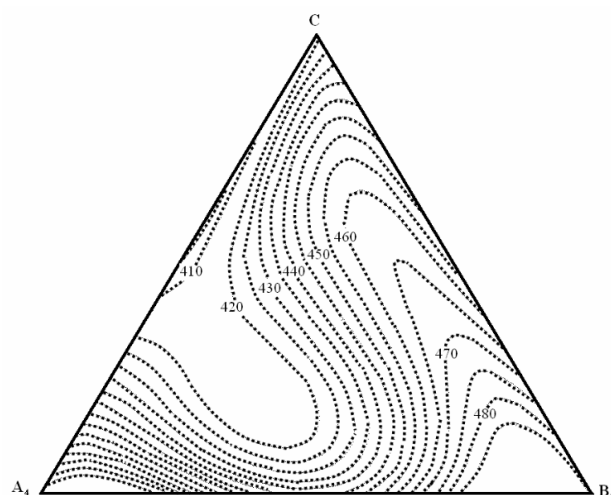
NPs, albeit asymmetric. From fig. 1 clearly shows the non-monotonic effect of each component on the size of nanoparticles in equilibrium with the solution.

To check the adequacy of equation 4 and establish the value of the Student's criterion, 4 additional solutions were prepared, the compositions of which are indicated in the table. 3

The discrepancy of 2–4 nm between the values of the absorption edge, calculated according to equation 2, and the experimental values indicates the high reliability of the functional dependence obtained by the fourth degree polynomial.

The results of TEM studies provided additional information about the shape, size, size distribution, and interparticle interactions in the investigated solutions (Fig. 3). The insets next to the TEM images show the size distribution diagrams of NPs obtained using the ImageJ computer program.

The calculated sizes of NPs from the values of the optical absorption edge according to formula 1 are given

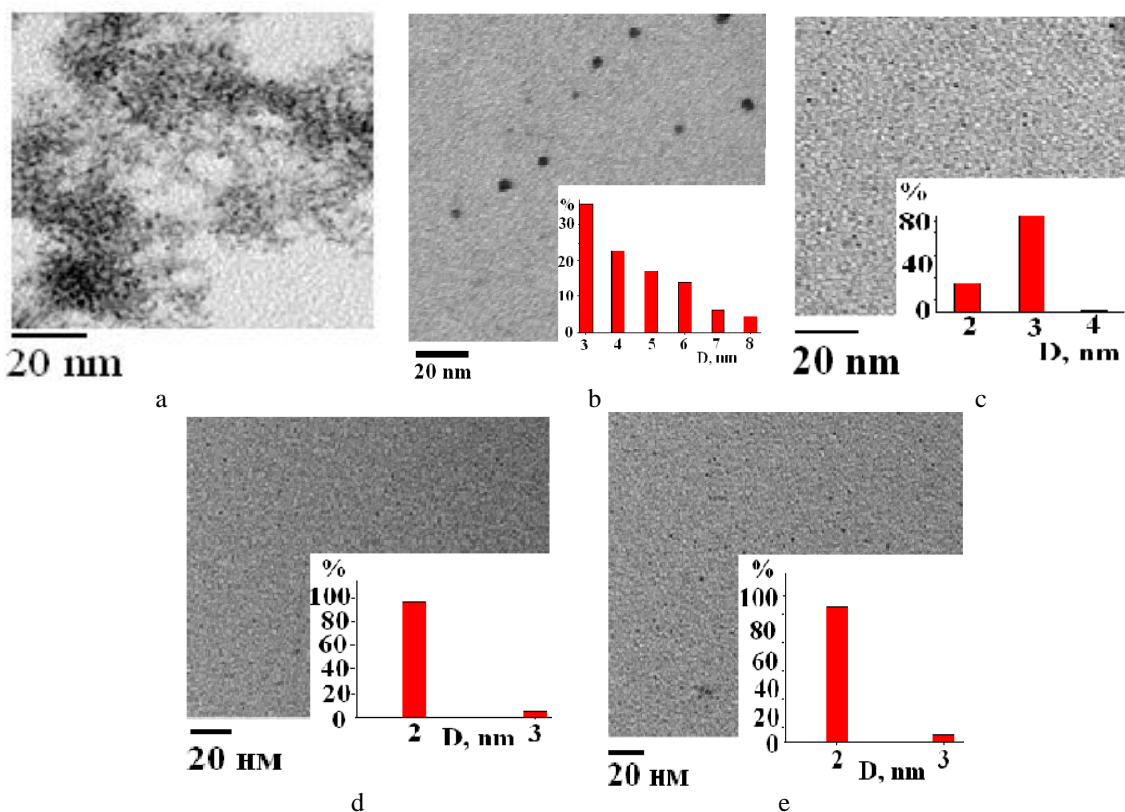


**Fig. 2.** Isolines of the absorption edge of solutions from the studied region  $A_4B_4C$  (interpolation by the fourth-degree approximation).

**Table 3.**

The results of the analysis of the adequacy of the model of optical research of solutions of the research area bounded by the triangle  $A_4B_4C$ .

№ π/π	The composition of the solution, fractions of a unit			$\lambda_{lim}$ ( $y_{ex}$ ), HM	$\lambda_{lim}$ ( $y_{cal}$ ), HM	$\Delta y$	$\zeta$	$t_{\omega/f}$
	$Cd^{2+}$	$S^{2-}$	L-Cys					
1	0.20	0.20	0.60	$454 \pm 7$	452	2	1.3	0.89
2	0.25	0.28	0.47	$450 \pm 8$	447	3	0.6	1.85
3	0.25	0.18	0.57	$447 \pm 7$	443	4	0.9	0.6
4	0.32	0.31	0.37	$437 \pm 5$	434	3	1.0	2.1



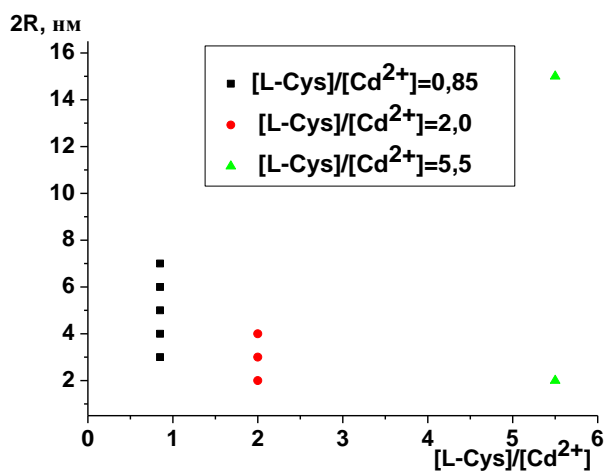
**Fig. 3.** TEM image of NPs from solutions №: a – 5; b – 11; c – 14; d – 3\*; e – 7\*

(3\* and 7\* - compositions of the system that do not belong to the 15 points according to the Scheffe plan but are within the study area). The insets show histograms of dispersion of NPs by size.

in table. Column 2 "2R, nm". According to TEM data, all synthesized NPs have a shape close to spherical, which confirms the validity of using formula 1 to estimate NP sizes. TEM images also confirm the conclusions made based on the data of optical studies about the small size of the obtained NPs (radius within 1.8 ~ 4 nm), which gives reason to consider them as quantum dots.

As can be seen from fig. 3, with a decrease in the stabilizer content in solutions with an equimolar content of  $\text{Cd}^{2+}$  and  $\text{S}^{2-}$  ions (Fig. 3 a, b, c), the size of NPs increases. With the same stabilizer content (Fig. 3, d and e), an identical excess of different ions (with a sufficiently high stabilizer content, 70%) causes similar effects: the solution is dominated by particles of the same size, but a high stabilizer content can enhance interparticle interaction, creating at the same time conditions for aggregation of NPs into clusters.

The general tendency to decrease the spread in the size of NPs with an increase in the ratio of the stabilizer content to the  $\text{Cd}^{2+}$  complexing agent (ie, the coordination number) is illustrated in Fig. 4.



**Fig. 4.** Size distribution of nanoparticles depending on the ratio ( $[\text{L-Cys}]/[\text{Cd}^{2+}]$ ).

Attempts to determine the type of crystal structure of the obtained NPs by x-ray methods did not yield unambiguous results. A similar problem was discussed in [10, 11], where it was established with the help of computer analysis that small ( $\varnothing < 5$  nm) CdS NPs are characterized by a special disordered structure, which is

different from the crystal structure of wurtzite and sphalerite, characteristic of bulk crystals of this semiconductor.

However, it can be assumed that the difference in the size and growth mechanisms of CdS NPs under the condition of an excess of ions of various types is related to the difference in the structure of the core of the NPs at the initial stages of growth. The presence of excess sulfide ions probably gives a hexagonal matrix with a more porous wurtzite structure. An excess of cadmium ions stimulates the growth of particles with a more densely packed structure, probably cubic.

## Conclusions

Using the method of mathematical planning of the experiment, the additive effect of the content of crystal-forming ions  $\text{Cd}^{2+}$  and  $\text{S}^{2-}$  and the stabilizer L-Cys on the process of formation of CdS/L-Cys nanoparticles under potentially oxidizing conditions (without deaeration of precursor solutions) and the optical properties of colloidal solutions obtained by pH = 7 conditions. On the "solution composition - absorption edge" diagrams, the concentration regions of existence of time-stable colloidal solutions of CdS/L-Cys NPs are established:  $\text{Cd}^{2+}$  – 10.0 – 47.5%; L-Cys – 30.0 – 80.0%;  $\text{S}^{2-}$  – 10.0 – 47.5%, and the influence of the content and ratio between precursors in the studied environment under stable synthesis conditions on the optical properties of NPs was determined.

The smallest particles (4 nm) are formed under the condition  $[\text{Cd}^{2+}]/[\text{S}^{2-}] \leq 3.5$ , which corresponds to the composition of  $\text{Cd}^{2+}$  systems – 10.0 – 35.0 %; L-Cys – 55.0 – 80.0 %;  $\text{S}^{2-}$  – 10.0 – 16.25 %. The value of the band gap of CdS/L-Cys NPs varies from 2.7 to 3.0 eV within the studied concentrations, the Stokes shift from 0.36 to 0.80 eV, while the optical absorption edge varies from 405 to 489 nm.

The use of the mathematical planning method in the synthesis and research of the three-component system  $\text{Cd}^{2+}$  -  $\text{S}^{2-}$  - L-Cys makes it possible to determine the conditions for the synthesis of CdS/L-Cys nanoparticles with given properties, in particular, their size.

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## Дослідження колоїдних розчинів CdS/L-цистеїну методом математичного планування

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В роботі досліджено адитивний вплив вмісту кристал-формуєчих іонів Cd<sup>2+</sup> і S<sup>2-</sup> та стабілізатора L-Cys із використанням методу математичного планування експерименту на процес формування наночастинок CdS/L-Cys в потенційно окислювальних умовах (без деаерації розчинів прекурсорів) та оптичні властивості колоїдних розчинів, одержаних за умови рН = 7 та температури 22°C. Статистичною обробкою результатів одержано рівняння та побудовано діаграми концентраційних залежностей довжини хвилі краю оптичного поглинання колоїдних розчинів наночастинок напівпровідника CdS в системі Cd<sup>2+</sup> – L-Cys – S<sup>2-</sup>.

**Ключові слова:** наночастинок (НЧ), математичне планування, оптичні властивості, діаграми залежності, концентраційна область.