Effect of the reaction mixture composition on CdS/L-cys nanoparticles optical properties

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L-cysteine-capped CdS nanoparticles were prepared by precipitation method in aqueous solution at room temperature, pH = 7 at ratio between precursor concentration taken in rather wide range. For the experimental results design, a mathematical planning according to simplex-lattice technique (Scheffe plan) was used that give a possibility to describe relationship between the properties and composition of multicomponent systems. The precursor content at the NP synthesis was ranged by 60 — 10 % Cd^{2+}, 80 — 30 % L-cys and 60 — 10 % S^{2-}. The nanoparticle size has been evaluated using the absorption spectra of the solutions. The general equations which describe absorption edge values depending on the solution composition are proposed.

Стабилизированные L-цистеином наночастицы CdS осаждены в водных растворах при комнатной температуре (pH = 7) при соотношениях между концентрациями прекурсоров, взятыми в широком интервале. Дизайн экспериментальных результатов проведен методом математического планирования по методике симплекс-решеток (Шеффе-план), позволяющей описать взаимосвязь между свойствами и составом многофункциональной системы. Содержание прекурсоров при синтезе наночастиц регулировалось в пределах 60 — 10 % Cd^{2+}, 80 — 30 % L-cys и 60 — 10 % S^{2-}. Размер наночастиц оценен по данным спектров поглощения полученных растворов. Предложены общие уравнения зависимости края поглощения от состава раствора.

1. Introduction

A^2B^6 nanoparticles (NP), especially, CdS have attracted great interest during the past two decades due to their unique electronic, optical, and catalytic properties [1–4]. CdS NP have been synthesized in numerous works via precipitation from aqueous solution using L-cysteine as stabilizing agents [3–9]. CdS nanoparticles capped with L-cysteine provide a new class of luminophors for use in chemical sensing, DNA sequencing, high throughput screening, and other applications. The cysteine amino acid passivates the CdS nanoparticles surface states more effectively than other thiols resulting in greater luminescence. CdS/L-cysteine NPs were found to be sensitive to certain physiologically important cations [5, 6]. Besides, it was described [7] an efficiency of such NP as biosensors, since biocompatible cysteine provides biologically active groups for possible targeting specific cell sites.

Various precursors (Cd^{2+}, S^{2-} and L-cys) concentration ratio were chosen by different authors for CdS/L-cys synthesis but lack of full clarity about correlation between the reaction system composition and the product properties.

Optical absorption spectroscopy of NP colloidal solutions was used mainly to measure the band gap and size of the nanoparticles. So, an useful attempt to adjust the CdS NP' band gap energy obtained from absorbance spectra as function of the synthesis parameters (concentration of stabilizer and sulfide source, pH of the system) based on a Statistical Design of Experiments was presented in [9]. The obtained correlations were visualized by 3D mathematical model.

The aim of this work is to reveal and describe the interrelation between the studied in wide range precursor content ratio and colloidal CdS/L-cys solutions absorbance spectra edge (λ_{edge}) using a mathematical planning technique for the experiments according to the Scheffe plan [10]. Such mathematical tool is usually used to determine the optimum combination of multicomponent system chemical constituents that provides a desired property using a minimum number of experimental runs. This approach also enables the number of experiments to be decreased to substantially reduce the time for the investigations.

2. Experimental

The L-cysteine capped CdS nanoparticles were deposited in aqueous medium using high purity precursors $CdCl_2 \cdot 2.5H_2O$ (Aldrich), L-cysteine (Fluka) and Na_2S (Aldrich). All experiments described in the paper were performed at pH = 7 before S^{2-} ions introduction into the reaction mixture.

The NaOH solution was introduced into the $CdCl_2$ and L-cysteine solutions mixture taken in ratio predicted by the Scheffe planning up to pH = 7 was attained. Then the estimated volume of Na_2S solution was added for CdS/L-cysteine nanoparticles formation following by H_2O adding up to the solution standard volume. The absorbance spectra of the obtained colloidal solutions were monitored at room temperature by USB-600 UV-spectrometer during not less than one month.

The planning of the experiments according to the simplex-lattice Scheffe model allows obtaining the analytical description of the relationship between the properties and the system composition with a continuous function. So, the change in the properties (y) as the function of the components content can be expressed with the polynomial of a certain degree with respect to the value of the n independent variables x_1, x_2, ..., x_n. The total empirical equation which describes the correlation "precursor content — system properties" for three-component system in forth degree approximation is as follows

$$y = k_1 x_1 + k_2 x_2 + k_3 x_3 + k_4 x_1 x_2 + k_5 x_1 x_3 +$$
$$+ k_6 x_2 x_3 + k_7 x_1 x_2 (x_1 - x_2) + k_8 x_1 x_3 (x_1 - x_3) +$$
$$+ k_9 x_2 x_3 (x_2 - x_3) + k_{10}(x_1 - x_2)^2 x_1 x_2 + \quad (1)$$
$$+ k_{11}(x_1 - x_3)^2 x_1 x_3 + k_{12}(x_2 - x_3)^2 x_2 x_3 +$$
$$+ k_{13} x_1^2 x_2 x_3 + k_{14} x_1 x_2^2 x_3 + k_{15} x_1 x_2 x_3^2,$$
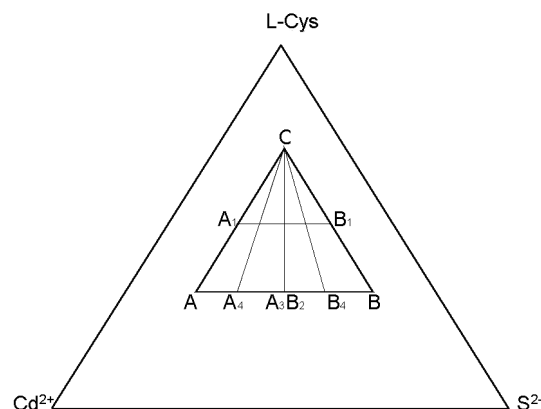

Fig. 1. Experimental region of the three-component mixture: point A is 60 % Cd^{2+}, 30 % Cys, 10 % S^{2-}; point B is 10 % Cd^{2+}, 30 % Cys, 60 % S^{2-} and point C is 10 % Cd^{2+}, 80 % Cys and 10 % S^{2-} .

where k_n is obtained from the experimental coefficients in predetermined points of the Scheffe plan; $x_{1,2,3}$ is concentration of each precursor. In our case x_1 corresponds to [Cd^{2+}], x_2 to [L-cys] and x_3 to [S^{2-}], respectively.

3. Results and discussion

Obviously, neither a pair Cd^{2+}-Cys nor a S^{2-}-Cys cannot result in formation of needed compound CdS. Therefore, there were used several approaches for the experiment planning. First step had required a choice of an initial triangle of the 3-component reactive system composition providing the formation NPs in a quantity sufficient for the absorbance spectra measurement. The view of the initial triangle ABC and particular triangles AB_2C, A_3BC and A_4B_4C position in the whole composition range is demonstrated by Fig. 1. The feasible regions are subsets within a simplex. The point A corresponds to the mixture of 60 % Cd^{2+}, 30 % Cys and 10 % S^{2-}. Point B is characterized by composition of 10 % Cd^{2+} + 30 % Cys + 60 % S^{2-}, and point C is ratio of 10 % Cd^{2+}, 80 % Cys and 10 % S^{2-}. The compositions of 15 experimental points pertinent to the triangle ABC according to the Scheffe plan and corresponding λ_{edge} values of the colloidal CdS NP solutions are shown as Table 1.

The calculated isolines with the same value of the λ_{edge} in the absorbance spectra of "fresh" solutions after 30–60 min holding at room temperature are illustrated in Fig. 2. Total equation for the data can be expressed as

Table 1

No. point	Precursor molar ratio			Solutions composition, %	λ_{edge}
	A	B	C		
1	1	0	0	$60Cd^{2+} + 30Cys + 10S^{2-}$	532
2	0.75	0	0.25	$47.5Cd^{2+} + 42.5Cys + 10S^{2-}$	545
3	0.5	0	0.5	$35Cd^{2+} + 55Cys + 10S^{2-}$	416
4	0.25	0	0.75	$22.5Cd^{2+} + 67.5Cys + 10S^{2-}$	413
5	0	0	1	$10Cd^{2+} + 80Cys + 10S^{2-}$	417
6	0	0.25	0.75	$10Cd^{2+} + 67.5Cys + 22.5S^{2-}$	448
7	0	0.5	0.5	$10Cd^{2+} + 55Cys + 35S^{2-}$	460
8	0	0.75	0.25	$10Cd^{2+} + 42.5Cys + 47.5S^{2-}$	473
9	0	1	0	$10Cd^{2+} + 30Cys + 60S^{2-}$	516
10	0.25	0.75	0	$22.5Cd^{2+} + 30Cys + 47.5S^{2-}$	483
11	0.5	0.5	0	$35Cd^{2+} + 30Cys + 35S^{2-}$	439
12	0.75	0.25	0	$47.5Cd^{2+} + 30Cys + 22.5S^{2-}$	467
13	0.5	0.25	0.25	$35Cd^{2+} + 42.5Cys + 22.5S^{2-}$	418
14	0.25	0.25	0.5	$22.5Cd^{2+} + 55Cys + 22.5S^{2-}$	445
15	0.25	0.5	0.25	$22.5Cd^{2+} + 42.5Cys + 35S^{2-}$	461

Table 2

No.	Solutions composition, fraction of unity			λ_{exp}, nm	λ_{calc}, nm	$\Delta\lambda = \lambda_{exp} - \lambda_{calc}$, nm	ζ	t
	x_1	x_2	x_3					
1	0.2	0.2	0.6	476	477.00	1.00	1.3	0.16
2	0.3	0.35	0.35	418	429.99	11.99	0.6	1.59
3	0.4	0.05	0.55	470	480.41	10.41	0.9	1.50
4	0.45	0.4	0.15	420	410.53	10.53	1.0	1.16

$$\lambda_{edge} = 417x_1 + 532x_2 + 516x_3 - 234x_1x_2 -$$
$$- 26x_1x_3 - 340x_2x_3 - 397x_1x_2(x_1 - x_2) +$$
$$+ 131x_1x_3(x_1 - x_3) - 128x_2x_3(x_2 - x_3) +$$
$$+ 1032(x_1 - x_2)^2x_1x_2 - 24(x_1 - x_3)2x_1x_3 +$$
$$+ 315(x_2 - x_3)^2x_2x_3 + 2848x_1^2x_2x_3 -$$
$$- 4259x_1x_2^2x_3 + 2237x_1x_2x_3^2. \qquad (2)$$

The adequacy and error of the model was tested using *t*-criterion [10, 11] according to the experimental data in four control points which are shown in Fig. 2 (as primed numbers). The appropriate results are illustrated in Table 2. The best coincidence (±1 nm) obtained in the ABC triangle center. The S^{2-} large excess causes deviation of the experimental value from the calculated one up to 10 nm that demonstrated satisfactory reliability of the results.
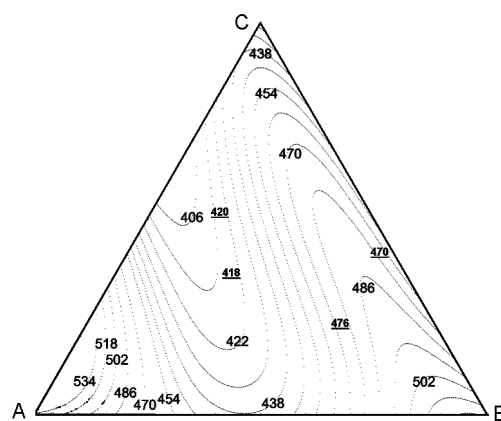

Fig. 2. Isolines of calculated λ_{edge} identical values in the large triangle ABC. The underlined numbers indicate excellent adequacy of the calculated and experimental data.

It is seen from Fig. 2 that at small excess of both the semiconductor components

and [Cys] = const (for example, along AC segment) the λ_{edge} value is shifted in long-way range but this occurs more evidently in Cd-rich side in comparison with S-rich one. Decrease of L-cysteine content at sulfur ions excess ($[S^{2-}]/[Cd^{2+}]\geq1$) along the BC segment regular shifts λ_{edge} in long-way range, from 417 to 516 nm. This corresponds to the nanoparticles size increase from 4 to 9 nm. A similar effect was observed at Cd^{2+} excess along the AC segment confirmed important role of the stabilizer as capping agent.

Since the solutions Nos. 1, 2 and 9 (see Table 1) were found unstable after one week storage (a solution turbidity was observed), three other restrictions on the components content were chosen, namely, AB_2C, A_3BC and A_4B_4C triangles. Therefore, the precursor content at the NP synthesis was ranged by 60 — 10 % Cd^{2+}, 80 — 30 % L-cys, and 60 — 10 % S^{2-}.

Total data about the solution stability at storage without direct lighting during one week combined in the large triangle ABC including the results from the AB_2C, A_3BC and A_4B_4C triangles are illustrated by Fig. 3. It can be concluded that the Cd^{2+} ion excess in the reaction mixture destabilizes the nanoparticles more evidently than the S^{2-} ion excess. So, gradual shift in the absorption edge in Cd-corner can be caused by cluster molecular aggregation. Basing on
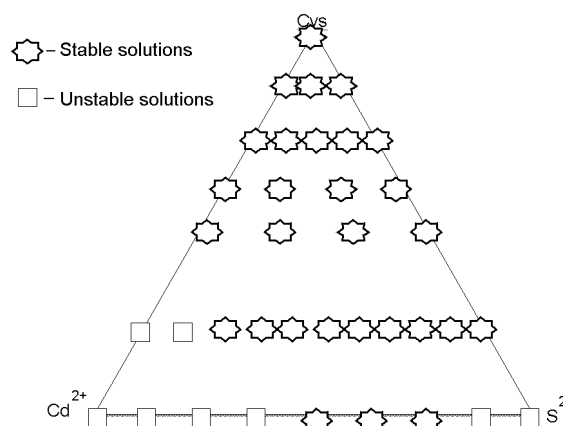

Fig. 3. Plan of stable (pick) and unstable (square) solutions of L-cysteine caped CdS nanoparticles (after one week storage at room temperature).

the obtained results, it was defined unstable solution composition range restricted by values 10 — 35 % Cd^{2+}, 30 — 42.5 % L-cys, 35 — 60 % S^{2-}. The range of stability can be restricted by 10–35 % Cd^{2+}, 30–80 % L-cys, 10–47.5 % S^{2-} points.

Taking into account this results, small A_1B_1C triangle of most stable solutions had been selected for the analytical description. It must be noted that the solutions with composition corresponding to this triangles attract attention also due to their high photoluminescence. The precursor composition

Table 3

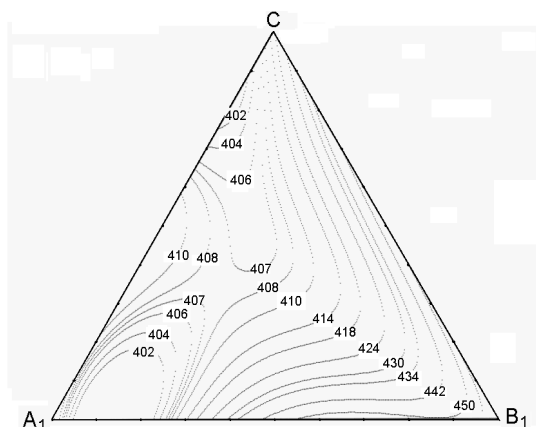| No. point	Precursor molar ratio			Solution composition. %	λ_{edge}
	A_1	B_1	C		
1	1	0	0	$60Cd^{2+} + 30Cys + 10S^{2-}$	532
2	0.75	0	0.25	$47.5Cd^{2+} + 42.5Cys + 10S^{2-}$	545
3	0.5	0	0.5	$35Cd^{2+} + 55Cys + 10S^{2-}$	416
4	0.25	0	0.75	$22.5Cd^{2+} + 67.5Cys + 10S^{2-}$	413
5	0	0	1	$10Cd^{2+} + 80Cys + 10S^{2-}$	417
6	0	0.25	0.75	$10Cd^{2+} + 67.5Cys + 22.5S^{2-}$	448
7	0	0.5	0.5	$10Cd^{2+} + 55Cys + 35S^{2-}$	460
8	0	0.75	0.25	$10Cd^{2+} + 42.5Cys + 47.5S^{2-}$	473
9	0	1	0	$10Cd^{2+} + 30Cys + 60S^{2-}$	516
10	0.25	0.75	0	$22.5Cd^{2+} + 30Cys + 47.5S^{2-}$	483
11	0.5	0.5	0	$35Cd^{2+} + 30Cys + 35S^{2-}$	439
12	0.75	0.25	0	$47.5Cd^{2+} + 30Cys + 22.5S^{2-}$	467
13	0.5	0.25	0.25	$35Cd^{2+} + 42.5Cys + 22.5S^{2-}$	418
14	0.25	0.25	0.5	$22.5Cd^{2+} + 55Cys + 22.5S^{2-}$	445
15	0.25	0.5	0.25	$22.5Cd^{2+} + 42.5Cys + 35S^{2-}$	461

Fig. 4. Isolines of calculated λ_{edge} identical values in the small triangle A_1B_1C.

field was restricted by the points presented in Table 3.

Coefficients in the equation which described the correlation "precursor content — λ_{edge} "for the triangle A_1B_1C with rather stable solutions are as follows

$$
\begin{aligned}
\lambda_{edge} = {} & 417x_1 + 416x_2 + 460x_3 - 14x_1x_2 + \\
& + 38x_1x_3 + 28x_2x_3 - 51x_1x_2(x_1 - x_2) + \\
& + 40x_1x_3(x_1 - x_3) - 139x_2x_3(x_2 - x_3) - \\
& - 157(x_1 - x_2)^2x_1x_2 + 8(x_1 - x_3)^2x_1x_3 - \\
& - 304(x_2 - x_3)^2x_2x_3 - 731x_1^2x_2x_3 + \\
& + 131x_1x_2^2x_3 - 1709x_1x_2x_3^2.
\end{aligned} \quad (3)
$$

Graphical interpretation of the equation (3) is presented in Fig. 4. According to the view, a slight blue shift in the absorption peak is observed with increase in L-cysteine concentrations, i.e., a decrease in the particles size. Probably, the growth of particles seems to be arrested because of increased Cd^{2+}-thiolate complexation on the surface of particles, which creates a steric barrier to aggregation.

As a deviation $\Delta\lambda = \lambda_{exp} - \lambda_{calc} = \pm1.5$ nm in this case was smaller in comparison with those for the large triangle ABC, this can be explained by higher stability of the solu-

tions from small triangle. Obviously for the obtaining of such functional correlations using the simplex-lattice method it is necessary to take into account the kinetic factors of the nanoparticles growth.

4. Conclusions

An improved mathematical method was used to analyse the interrelation between the precursor ratio studied in wide range and colloidal CdS/L-cys solutions absorbance spectra edge (λ_{edge}) using a simplex-lattice planning technique according to the Scheffe plan. The absorbance properties of the observed three-component system can be described by adequate equations with consideration of the solutions tendency to the nanoparticles aggregation. Composition ranges for stable solutions (10–35 % Cd^{2+}, 30–80 % L-cys, 10–47.5 % S^{2-}) and unstable ones (10 – 35 % Cd^{2+}, 30 – 42.5 % L-cys, 35 – 60 % S^{2-}) were obtained.

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Вплив складу реакційної суміші на оптичні властивості наночастинок CdS/L-цистеїн

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Стабілізовані L-цистеїном наночастинки CdS осаджено у водних розчинах при кімнатній температурі (pH = 7) при співвідношенні між концентраціями прекурсорів у широкому інтервалі. Для дизайну експериментальних результатів використано метод математичного планування за методикою симплекс-граток (Шеффе-план), що дає можливість описати взаємозв'язок між властивостями і складом багатофункціональної системи. Вміст прекурсорів при синтезі наночастинок регулювався у межах $60 \div 10$ % Cd^{2+}, $80 \div 30$ % L-cys і $60 \div 10$ % S^{2-}. Розмір наночастинок оцінено за даними спектрів поглинання отриманих розчинів. Запропоновано загальні рівняння залежності краю поглинання від складу розчину.