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Preparation and Study of Colloid-Chemical and Optical Properties of the Nanocrystals of Zinc Sulfide Modified with Amino Acids

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Abstract—The effect of some amino acids: cysteine, methionine, glycine, lysine, and aspartic acid, on the formation of nanoparticles of zinc sulfide in aqueous solutions at pH 5.5–10.0 was investigated. A method of obtaining stable sols of ZnS particles of 2–4 nm size with narrow distribution of the particle size was developed. The investigated nanoparticles are shown to be sphalerite, the cubic modification of zinc sulfide. The ZnS sols modified with methionine and glycine show intense luminescence at 415–425 nm.

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Chalcogenides of some transition metals, in particularly zinc, cadmium, and lead, belong to the most widespread and well studied semiconductor materials capable of luminescence under optical or electric excitation. In recent years, interest in these substances increased owing to the obtaining of the so-called quantum dots, the crystals of the several nanometers size, with unique optical properties. It is expected that this material will be widely used as fluorescent tags in the identification systems and medical diagnostics, the light emitting diodes, in the optical and electronic devices, and in several other areas.

For obtaining the nanoparticles of the transition metals chalcogenides a variety of approaches is used. We mention only some: pyrolysis of organometallic compounds [1], ultrasound dispersion [2], mechanochemical method [3], and the most popular methods of their synthesis in inverse micelles [4, 5] and microemulsions [6, 7]. Unfortunately, most existing methods cannot simultaneously solve two major problems: a synthesis of nanoparticles with a fairly narrow particle size distribution and producing the nanoparticles in a preparative amount that is important in the light of their practical use. We have to mention also the general problem in the nanotechnology: stabilization of nanodispersed particles and prevention of the nanoparticles aggregation.

Earlier [8], we proposed a general method for the synthesis of nanoparticles of water-insoluble crystalline compounds. This method, which we named a double drop procedure, is the gradual addition of reagents to a large volume of reaction solution. The formation of crystallites takes place at high dilution and at the same concentration for each new portion of the reagents. This should facilitate the formation of particles of small size with narrow dispersion by size.

An effective method to stabilize the colloidal particles formed is adding a modifier capable of the chemisorption on the particle surface. In [8] we used cysteine and dodecanethiol to stabilize the particles of copper(II) sulfide. The presence of HS groups in the molecules of these modifiers provides a strong fixation of the molecules on the surface due to the formation of coordination bond with the surface metal ions. A similar approach based on these and other mercapto-containing modifiers was used also in the works of other researchers [9–12].

However, modifiers with HS groups have a number of disadvantages, one of which, paradoxically, is the high strength of bonding that can interfere in some cases with the processes of further transformation of the particles and manipulation with them. Furthermore, the mercapto group is easily oxidized by atmospheric oxygen.

Table 1. Influence of modifier and pH on the stability of ZnS sols and content of modifier in the particles formed

Modifier	pH	ZnS threshold concentration, M × 10^{-3}	Carbon content, %
–	10.0	<0.8	0.54
Cysteine	10.0	>60	13.3
	8.5	24	12.4
	7.0	3.8	10.9
	5.5	<0.8	10.4
Methionine	10.0	10	1.99
	8.5	4	–
	7.0	<0.8	0.56
	5.5	<0.8	–
Glycine	10.0	10	–
	8.5	2	–
	7.0	<0.8	–
	5.5	<0.8	–
Lysine	10.0	<0.8	6.25
	8.5	<0.8	0.94
	7.0	<0.8	0.39
	5.5	<0.8	1.12
Aspartic acid	10.0	3	1.78
	8.5	<0.8	1.62
	7.0	<0.8	1.49
	5.5	<0.8	2.09

In this paper we present the data on the effect of other amino acid modifiers on the formation of nanoparticles in aqueous solutions and their colloid-chemical characteristics and optical properties. As an object of the study zinc sulfide was selected.

The choice of amino acids as modifiers of the zinc sulfide surface was defined by the fact that they are capable to form sufficiently stable complexes with zinc ions. In addition, the natural amino acids bearing different functional groups that can contribute both to the binding to the surface and stabilization of the formed colloidal systems are accessible and relatively inexpensive.

In the present work the following L-amino acids were used as modifiers: cysteine $HSCH_2CH(NH_2)COOH$, methionine $CH_3SCH_2CH_2CH(NH_2)COOH$, glycine $CH_2(NH_2)COOH$, lysine $NH_2(CH_2)_4CH(NH_2)\cdot COOH$, and aspartic acid $HOOCCH_2CH(NH_2)COOH$.

In the first stage of this work we studied the effect of pH on aggregate stability of the ZnS-amino acid sols. For this purpose to the solutions of amino acids at different pH by double-drop method at continuous stirring were added 0.5 M solutions of $ZnSO_4$ and Na_2S. At the beginning of the experiments (with low content of the resulting ZnS) formed sols, and at a certain threshold concentration occurred precipitation, which was registered visually.

Table 1 shows the results of observations indicating that the decrease in pH from 10.0 to 5.5 lowers the threshold concentration of ZnS, which indicates a decrease in aggregative stability of sols. This trend is most clearly evident for the system of ZnS–cysteine. In this case the falling of the ZnS threshold concentration upon decrease in pH is over two orders of magnitude.

By analogy with the CuS–cysteine system it is presumable that the fixation of cysteine on the surface of ZnS is due to the interaction of HS-groups with the zinc ions in the crystal lattice, and the remaining free amino acid group (–COOH and–NH_2 groups) defines the surface charge of the particle. At pH 10, this charge is negative; at approaching the isoelectric point of cysteine pI = 5.02 [13] the charge is reduced to zero, which leads to particle aggregation and precipitation.

The second factor affecting the stability of the sols is the modifier efficiency of binding, or its surface concentration. The HS-group of cysteine forms stronger complexes with the zinc ion than the methionine CH_3S group, which defines a higher stabilizing ability of cysteine (see Table 1).

The third factor that must be taken into account when analyzing the data of Table 1 is the difference in the mechanism of binding modifiers. In contrast to cysteine and methionine, sorption of glycine, lysine, and aspartic acid could be due only to amino acid groups. In homogeneous solution the complexes of amino acids with transition metal ions are of chelate structure with the simultaneous coordination of amino and carboxy groups. It is not obvious that such a structure can be realized on a planar crystal face, where the metal ion has only one free coordination site. It can be assumed that the chelate complexes are formed on the edges of the nanocrystal and on the various defects, whereas in other parts of the surface the binding will be implemented on the one group of amino acid only, most likely the carboxy group. An indirect confirmation of this statement is quite a high stability of the ZnS-glycine system, since at the bidentate binding of glycine there are no groups on the surface capable of ionization.

For the characterization of the particles form they were precipitated from the sol, washed, and studied by

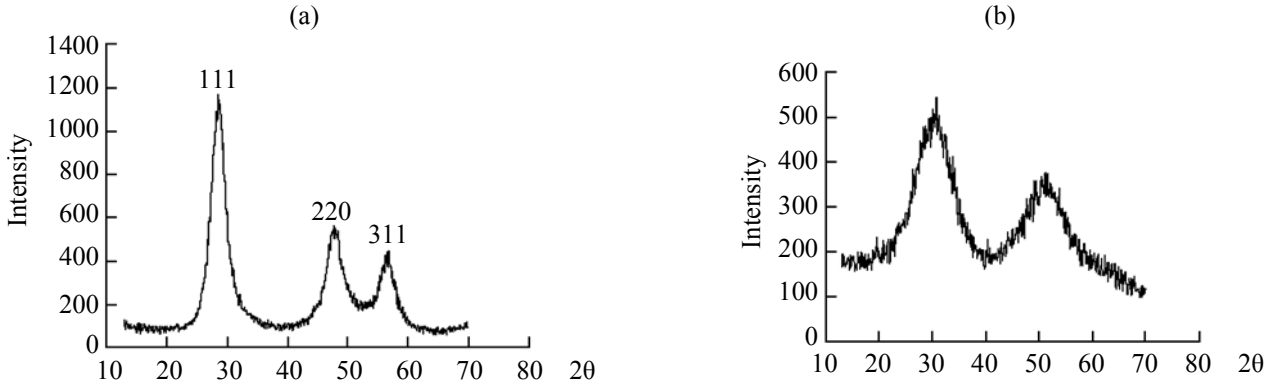

Fig. 1. Powder X-ray pattern of unmodified (a) ZnS and (b) ZnS, synthesized at pH 10 in the presence of cysteine.

the methods of elemental analysis, (Table 1), X-ray phase and X-ray diffraction analyses (Fig. 1). Diffraction patterns of the samples are characterized by the presence of three diffuse diffraction peaks, (111), (220), and (311), corresponding to the cubic modification of ZnS (sphalerite). The appearance of diffraction patterns indicates the presence of many defects in the fine crystalline structure of the investigated objects. Comparison of diffraction patterns of the original (Fig. 1a) and the modified with cysteine (Fig. 1b) samples of zinc sulfide shows decrease in the intensity of reflexes, increase in the line broadening and increase in the noise level. This indicates an increase in disordering the cubic phase and increase in the content of X-ray-amorphous component. The average particle size of unmodified and modified samples was calculated by the Selyakov–Scherrer formula (Table 2). A comparison of these values shows a significant effect of the modifier not only on the aggregate stability of sols formed, but also on the particle size, which, according to the X-ray data varies from 6.0 to 2.0 nm. The modifier adsorption on the surface of the particles reduces the excess surface energy and prevents further growth of the particles. This effect is most clearly evident in the case of cysteine possessing the highest affinity for zinc ions: image size of crystallites formed in the presence of this modifier decreases 3-fold compared with unmodified samples.

From the data on the elemental analysis (Table 1) and the average particle size (Table 2), we estimated the surface concentration of adsorbed modifier (in the approximation of spherical particles). It amounted to the following values: cysteine 3.0, lysine 1.0, methionine 0.5, aspartic acid 0.6 molecule nm^{-2}. These values are typical for the processes of monolayer chemical modification of various surfaces [14].

The average diameter of particles in the precipitate were also evaluated using transmission electron microscopy. The results are in satisfactory agreement with the X-ray diffraction data (Table 2). From the data in Table 2 is also seen that the pH of the solution in the synthesis has virtually no effect on the size of the particles.

Size characteristics of ZnS particles in the sols were obtained by dynamic light scattering, the results are shown in Figs. 2 and 3 and in Table 2. As follows from the data obtained, in the system of ZnS–cysteine the sol consisting of primary particles can be obtained in

Table 2. Effect of modifier and pH on the zinc sulfide average particle size

Modifier	pH	The average particle size, d_{av}, nm		
		in ash, according to DLC	in precipitate, according to TEM	in precipitate, according to the RFA
–	10.0	–	3.5±0.9	6.0±0.3
Cysteine	10.0	2.7±0.2	1.7±0.2	2.0±0.1
	8.5	2.6±0.1	2.4±0.6	–
	7.0	2.6±0.2	2.1±0.3	–
	5.5	–	2.0±0.5	–
Methionine	10.0	5.5±0.8	5.0±2.0	4.0±0.2
	8.5	13.5±0.6	5.0±2.0	–
Glycine	10.0	11.3±0.2	5.0±2.0	4.0±0.2
	8.5	14.8±0.8	4.0±1.0	–
Lysine	10.0	–	3.1±0.6	–
Aspartic acid	10.0	–	4.0±1.0	–

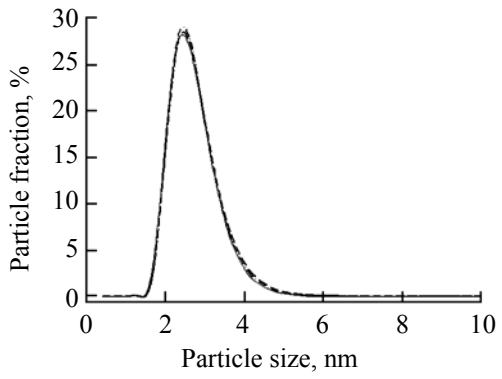

Fig. 2. Particle size distribution in the systems ZnS–cysteine, obtained at pH 10.0, pH 8.5, and pH 7.0.

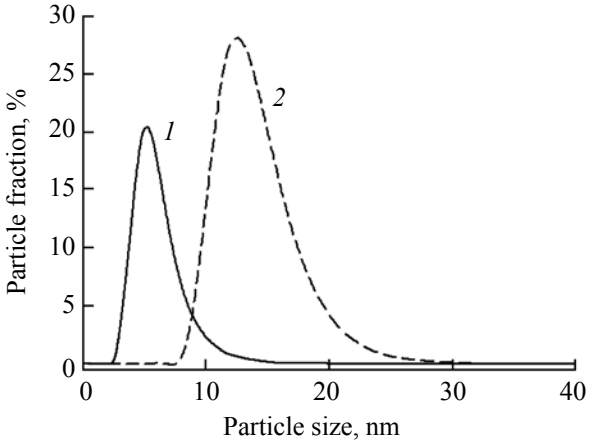

Fig. 3. Particle size distribution in the systems ZnS–methionine obtained at pH (*1*) 10.0 and (*2*) 8.5.

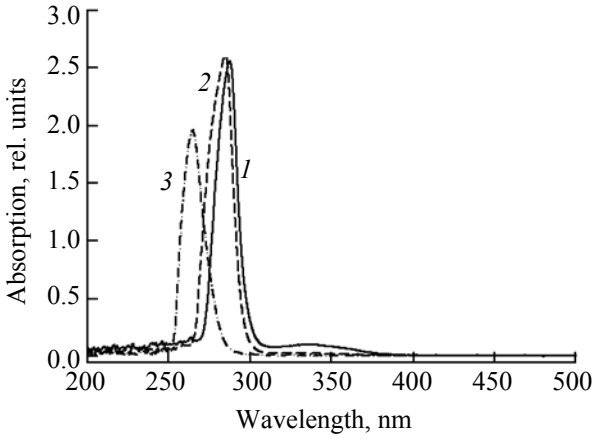

Fig. 4. Absorption spectra of ZnS–cysteine sols obtained at pH (*1*) 10.0, (*2*) 8.5, and (*3*) 7.0.

the entire investigated range of acidity. In other systems an increase in acidity leads to the association of primary particles with the formation of associates of 11–15 nm size, although these systems are also characterized by relatively narrow particle size distribution. Note that in the absence of modifier the primary particles of zinc sulfide in a similar situation almost instantly associated and precipitated.

More information about the structure of nanoparticles formed by zinc sulfide can be obtained from the analysis of their optical properties.

Figure 4 shows the absorption spectra of the ZnS–cysteine sols obtained at different values of pH. The systems synthesized at pH 10.0 and 8.5 are characterized by narrow absorption bands with very similar absorption maxima, λ_{max} = 286 and 284 nm, respectively. Therewith, the position of maximum absorption of the sample obtained at pH 7.0 is shifted to the blue region: λ_{max} = 265 nm.

From the data of [15] it is known that a decrease in the size of ZnS particles leads to a shift of the absorption maximum to shorter wavelengths. However, using the methods of dynamic light scattering and transmitting electron microscopy we found that the sizes of zinc sulfide particles in the cysteine sols remain unchanged and not dependent on the pH. Apparently, the shift of the absorption maximum is due to greater sensitivity of UV spectroscopy to particle size compared with the methods of the DLC and TEM that do not allow the detection of the changes.

Unlike the cysteine system, for the systems ZnS–methionine and ZnS–glycine the absorption in a wide range of wavelengths is characteristic (see Fig. 5). If we accept the statement that the absorption wavelength is defined mainly by the particle size, the significant broadening of the absorption band should be ascribed to the wider distribution of particle size in the systems of ZnS–methionine and ZnS–glycine.

Another principal difference of the ZnS–methionine and ZnS–glycine systems from the cysteine system is the presence in two former of intense blue photoluminescence. Position of the luminescence maximum is approximately the same for all the samples and corresponds to 415–425 nm (Fig. 6). Some authors attribute the appearance of this band to the self-activated luminescence of zinc sulfide due to intrinsic point defects of the ZnS lattice [12, 16, 17].

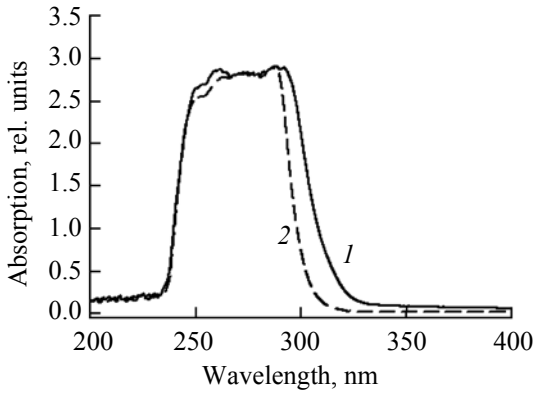

Fig. 5. Absorption spectra of ZnS–methionine systems obtained at pH (*1*) 10.0 and (*2*) 8.5.

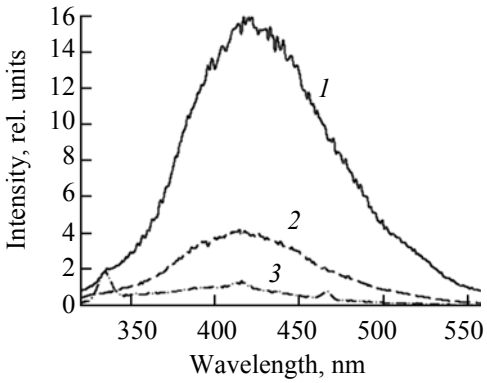

Fig. 6. Photoluminiscence spectra of ZnS–methionine systems obtained at pH (*1*) 10.0, and (*2*) 8.5, and (*3*) background; λ_{ext} = 300 nm, T = 298 K.

Besides, it was found that adding cysteine to the ZnS–methionine system leads to a significant reduction in the luminescence intensity due apparently to the gradual replacing methionine by cysteine on the surface of zinc sulfide. Inhibitory effect of cysteine may be due to its high affinity for zinc ions and high surface concentrations, which lead to more efficient binding to the defects on the surface of the ZnS particle. Also, the electron-acceptor properties of HS-group should be taken into account, which may lead to a decrease in the proportion of free carrier in the semiconductor nanocrystal.

In general, we can conclude that the use of amino acids as modifiers of nanoparticles of zinc sulfide is an effective instrument for regulating the size of particles formed, aggregative stability of sols, and optical characteristics of nanoparticles.

EXPERIMENTAL

We used $ZnSO_4 \cdot 7H_2O$ (pure grade), $Na_2S \cdot 9H_2O$ (Sigma Aldrich, 99%), L-cysteine hydrochloride monohydrate (Fluka, chemically pure grade), L-methionine, L-Lysine hydrochloride, aspartic acid, glycine (Reanal, chemically pure grade). To prepare working solutions in all experiments distilled water was used. All the experiments and studies of physical and chemical characteristics of the objects of research were carried out at room temperature.

Preparation of modified ZnS. Zinc sulfide was obtained from 0.5 M solutions of $ZnSO_4$ and Na_2S by the double drop method with simultaneous dilution of the initial reagents to the reaction concentration 10^{-3} M [8]. In a beaker containing 19 ml of a solution of respective amino acid ($C = 7.2 \times 10^{-2}$ M) at a given pH value (10.0, 8.5, 7.0 or 5.5) were added from two burettes simultaneously the reagents in an equal quantity, while stirring the reaction mixture with a magnetic stirrer. For the deposition of zinc sulfide obtained in the solution of cysteine at pH 10, to the system was added a few drops of 10% solution of acetic acid. The precipitate obtained was centrifuged, washed with distilled water 4–5 times, and dried in air.

The obtained samples of zinc sulfide were investigated by the following physicochemical methods.

Transmission electron microscopy. Micrographs of samples were recorded on a transmission electron microscope LEO912 AB OMEGA (accelerating voltage 60, 80, 100, 120 kV; the field of lighting 1 to 75 μm; the aperture of illumination 0.02–5 mrad; zoom from ×80 to ×500 000; image resolution from 0.2 to 0.34 nm, energy resolution of inelastic scattering 1.5 eV; region of measuring the energy of the inelastic scattering 0–2500 eV).

Dynamic light scattering (JEM). Measurement of particle sizes in colloid solutions was carried out using dynamic light scattering on a Zetasizer Nanoseries (Nano-ZS) instrument of Malven company. Light source is a helium–neon laser, the wavelength of the incident light 633 nm. Measurement was carried out in a temperature-controlled cell with optical path of 10 mm length, at 20°C.

Elemental analysis. Determination of carbon in the samples was performed by burning a sample in a rapid stream of oxygen by the method of [18].

Spectral methods. The absorption and luminescence spectra of zinc sulfide nanoparticles in

solutions of amino acids were recorded in quartz cells with an optical layer thickness of 10 mm on a Flyuorat-02-Panorama spectrofluorimeter of Lumex Company, Ltd. The wavelength of luminescence excitation was chosen on the basis of the obtained absorption spectra.

X-ray phase analysis. X-ray phase analysis (XPA) of the samples was performed on a diffractometer Stoe Stad P for powders in the θ/θ geometry with the CuK_α-radiation. Registration was carried out in the range of angles 15–70° (2θ scale) with the increment 0.05° and exposure 10 s per a point.

To determine the average size of the coherent scattering regions (COR) an approximation method was used based on the analysis of the integral width of diffraction peaks. To estimate the size of the sphalerite COR diffraction maximum (111) was recorded with step 0.05 and time 50 s per point.

The average COR size was estimated by the Selyakov–Scherrer formula: $D = \lambda/(\beta\cos\theta)$, where λ is X-ray emission wavelength (nm), β is physical broadening (rad), θ is Wulf–Bragg angle. The error of the COR estimation was 5.7%.

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REFERENCES

1. Murray, C.B., Norris, D.J., and Bawendi, M.G., *J. Am. Chem. Soc*., 1993, vol. 115, no. 19, p. 8706.
2. Xu, J. and Wei, Ji., *J. Mater. Sci. Lett*., 1999, vol. 18, p. 115.
3. Balaz, P., Boldizarova, E., Godocikova, E., and Briancin, J., *Mater. Lett*., 2003, vol. 57, p. 1585.
4. Liveri, V.T., Rossi, M., D'Arrigo, G., Manno, D., and Micocci, G., *Appl. Phys., A*, 1999, vol. 69, p. 369.
5. Summ, B.D. and Ivanova, N.I., *Usp. Khim*., 2000, vol. 69, no. 11, p. 995.
6. Ivanova, N.I., Rudelev, D.S., and Summ, B.D., *Vestn. Mosk. Univ., Ser. 2, Khimiya*, 2001, vol. 42, no. 6, p. 405.
7. Lopez-Quintela, M.A. and Rivas, J., *J. Colloid Interface Sci*., 1993, vol. 158, p. 446.
8. Zhilenko, M.P., Erlikh, G.V., and Lisichkin, G.V., *Ros. Nanotekhnologii*, 2009, vol. 4, nos. 5–6, p. 83.
9. Bae, W. and Mehra, R.K., *J. Inorg. Biochem*., 1998, vol. 70, p. 125.
10. Kho, R., Torres-Martinez, C.L., and Mehra, R.K., *J. Colloid Interface Sci*., 2000, vol. 227, p. 561.
11. Wageh, S., Ling, Z.S., and Xu-Rong, X., *J. Cryst. Growth*, 2003, vol. 255, p. 332.
12. Li, H., Shih, W.Y., and Shih, W.-H., *Nanotechnology*, 2007, vol. 18, p. 205604.
13. Jakubke, H.-D. and Jeschkeit, H., *Aminokysloty, peptidy, belki* (Amino Acids, Peptides, and Proteins), Moscow: Mir, 1985, p. 32.
14. *Khimiya privitykh poverkhnostnykh soedinenii* (Chemistry of Grafted Surface Compounds), Lisichkin, G.V., Ed., Moscow: Fizmatlit, 2003.
15. Wageh, S., Liu, Shu-Man, Fang, Tian You, and Xu, Xu-Rong., *J. Lumin*., 2003, vols. 102–103, p. 768.
16. Morozova, N.K. and Kuznetsov, V.A., *Sul'fid tsinka. Poluchenie i opticheskie svoistva* (Zinc Sulfide. Preparation and Chemical Properties), Moscow: Nauka, 1978.
17. Becker, W.G. and Bard, A.J., *J. Phys. Chem*., 1983, vol. 87, p. 4888.
18. Klimova, V.A., *Osnovnye mikrometody analiza organicheskikh soedinenii* (Basic Micromethods of Analysis of Organic Compounds), Moscow: Khimiya, 1975.