Russian Chemical Bulletin, International Edition, Vol. 59, No. 7, pp. 1307—1311, July, 2010

Preparation of copper and zinc sulfide nanoparticles and their modification with cysteine

M. P. Zhilenko,* K. V. Lupandina, H. V. Ehrlich, and G. V. Lisichkin

Department of Chemistry, M. V. Lomonosov Moscow State University,
1 Leninskie Gory, 119991 Moscow, Russian Federation.
Fax: +7 (495) 932 8846. E-mail: zhilenko@petrol.chem.msu.ru

A new method for the preparation of copper and zinc sulfides nanoparticles in homogeneous aqueous solutions using cysteine as a surface modifier was proposed. The size of the particles obtained is 5—7 and 1.5—3 nm for copper and zinc sulfides, respectively, depending on the concentration of the reactants. Associates of the nanoparticles 10—30 nm in size are formed in the system with an increase in the total concentrations of the sulfides. Sols of the nanoparticles obtained in cysteine solutions are resistant to oxidation and coagulation within several weeks. The variation of the synthesis conditions makes it possible to obtain zinc sulfide particles with optical properties related to size effects.

Key words: nanoparticles, metal sulfides, surface modification, cysteine, stability, size effects.

One of the main problems of nanotechnologies is the preparation of nanoparticles with specified shape and size and rather narrow size distribution, as well as their isolation, fractionation, and purification. Without solving this problem nanotechnologies will not become real technologies but will be involved in the infinitely lasting process of scientific research of the nanosized state of substances.

An example is the popular method for the preparation of nanodispersed semiconducting metal sulfides in organic media in reverse micelles, so-called nanoreactors (see, *e.g.*, Refs 1 and 2). Specifics of similar colloidal systems makes it possible to work at concentrations of the starting and final substances of an order of 10^{-5} mol L^{-1}, which sharply restricts possibilities of the technological use of this method. In addition, problems concerning the isolation and purification of the particles formed from the components of the reaction medium arise.

We have earlier[3] used an original procedure of mixing the reactants and modifying agent, which makes it possible to obtain copper sulfide nanocrystals 5—10 nm in size in an aqueous solution with their resulting concentration in the system about 10^{-2} mol L^{-1}. The essence of the double dropping method used is the slow simultaneous addition of concentrated solutions of copper chloride and sodium sulfide (0.5 mol L^{-1}) to a multiply large volume of an aqueous solution. Upon feeding of each portion of the reactants, they are diluted by 3—4 orders of magnitude and copper sulfide is formed at low concentrations, resulting in the formation of nanosized crystallites. In addition, each new portion of copper sulfide is formed under the same conditions of absence of excess of Cu^{2+} and S^{2-}, which are capable of specific adsorbing on the surface of the nanocrystals formed, and the dilution of the starting solutions remains almost unchanged during the whole synthesis.

The most important role in the procedure developed belongs to the modifying agent. We used[3] dodecanethiol as a modifying agent. The modifier is chemisorbed on the surface of nanocrystals formed, thus preventing their further growth and aggregation and protecting them from oxidation during isolation and storage. In addition, the change in the hydrophilic particle surface by the hydrophobic one allows one to extract them with nonpolar solvents, remaining excesses of the starting and formed inorganic salts in the aqueous phase. Organic solvents are easily removed by distillation, and the powders obtained can be stored for a long time. If necessary, nanosized crystals of copper sulfide can be redispersed in an organic medium.

The present work is the next step in the development of the method proposed. The use of hydrophilic ionogenic substances as modifying agents, which allows one to perform the process in a homogeneous medium, is of doubtless interest. We used amino acid cysteine $HSCH_2CH(NH_2)COOH$ as such a modifier. We believed that the thiol group of cysteine would provide the strong fixation of the modifier on the nanoparticle surface due to the high affinity of transition metal ions to sulfur-containing ligands and the ionogenic amino acid group would enhance the aggregative stability of the particles due to the electrostatic repulsion. Zinc sulfide widely used as a luminophore was chosen as the object of the study along with copper sulfide.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 7, pp. 1277—1281, July, 2010.

1066-5285/10/5907-1307

Together with the synthetic aspect, we were interested in general regularities of chemical modification of the surface of ionic crystals, which, unlike the chemical modification of the surface of metals and oxides (see, *e.g.*, Ref. 4), remain almost unstudied. In addition, these studies can be useful for investigation of the conditions of formation of bionanoparticles formed in living organisms (see, *e.g.*, Refs 5 and 6).

Experimental

We used $CuSO_4 \cdot 5H_2O$ (reagent grade, Khimmed), $ZnSO_4 \cdot 7H_2O$ (pure, Khimmed), $Na_2S \cdot 9H_2O$ (99%, Aldrich), L-cysteine hydrochloride monohydrate (Fluka). In all experiments, distilled water was used for the preparation of working solutions.

Sizes of the obtained particles were determined by transmission electron microscopy (TEM) in precipitates and by dynamic light scattering (DLS) in sols.

The particles sizes in colloidal solutions were measured by the dynamic light scattering method on a Zetasizer nanoseries instrument (Nano-ZS, Malven). The light source was a helium—neon laser with an incident light wavelength of 633 nm. The measurements were carried out in a temperature-controlled cell with an optical path thickness of 10 mm at 20 °C.

Absorption spectra of sols of copper and zinc sulfides in cysteine solutions and in washing waters of some precipitates were recorded in quartz cells (10 mm) on a Specord UV-VIS spectrophotometer.

X-ray photoelectron spectra (XPS) were measured on a LAS-3000 instrument (Riber) equipped with an OPX-150 semispherical analyzer. For the excitation of photoelectrons, we used the non-monochromatized X-ray radiation of an aluminum anode ($AlK_\alpha = 1486.6$ eV) with a voltage on the tube of 12 kV and an emission current of 20 mA. Photoelectron peaks were calibrated by the carbon line C1s with the bond energy (E_b) 285 eV. Vacuum in the working chamber was $5 \cdot 10^{-10}$ Torr. A ionic pump was used to obtain high vacuum.

The carbon content in the samples was determined by burning the substance in a fast oxygen current according to a published method.[7]

Synthesis of unmodified copper and zinc sulfides. Copper and zinc sulfides were synthesized from aqueous solutions of $CuSO_4$ or $ZnSO_4$ and Na_2S with the initial concentration 0.5 mol L^{-1} using the double dropping method at room temperature. Equal volumes of the starting reactants were simultaneously added dropwise from two burettes with continuous stirring to a flask containing a necessary amount of distilled water. The water volume in the flask was calculated from the volumes of droplets in the burettes in such a way that the dilution of each droplet to 10^{-3} or 10^{-4} mol L^{-1} was provided. The precipitates obtained were centrifuged, washed with water 3—5 times, and dried in air to a constant weight.

Synthesis of copper and zinc sulfides in the presence of cysteine. Solutions of Na_2S and $CuSO_4$ or $ZnSO_4$ (0.3—5 mL each) with a concentration of 0.5 mol L^{-1} were added to an aqueous solution of cysteine (pH 10) at room temperature with continuous stirring using the double dropping method. The volume of the cysteine solution was calculated analogously to the procedure described above. The mole amounts of cysteine in the solution corresponded to the mole amounts of CuS or ZnS formed in experiment. After the addition of solutions of $CuSO_4$ or $ZnSO_4$, the reaction mixture was stirred for 2—3 h. The precipitates that formed were filtered off, washed with water several times, and dried in air.

Results and Discussion

The first stage of the present work was the study of the dependences of the size of unmodified copper and zinc sulfide particles on the concentrations of the starting reactants in the reaction medium. The reaction concentrations were varied in the range from 10^{-4} to 10^{-3} mol L^{-1} in which according to Ref. 3, stable sols of nanoparticles are formed. It should be mentioned that it is very inconvenient to obtain a preparative (tens of milligrams) amount of CuS and ZnS, which is sufficient for studying by the most part of physicochemical methods, from the starting solutions of the corresponding salts with so low concentrations, because in this case it is necessary to use large (liter) volumes of the starting reactants. This is one of advantages of the proposed by us double dropping method, which makes it possible to achieve any high dilutions of the starting reactants at relatively small (200—500 mL) solution volume in the reaction vessel. In addition, the slow and gradual increase in the content of metal sulfide particles in the reaction medium allows one to detect its threshold concentration, exceeding of which results in precipitation from the sol.

According to the TEM data, all obtained precipitates of CuS and ZnS represent aggregates consisting of primary particles. The mean sizes of the primary copper sulfide particles are appreciably larger than those of zinc sulfide (Table 1). In the both cases, the mean sizes of the particles increase with an increase in the reaction concentration of the corresponding reactants.

The CuS and ZnS precipitates are formed from sols at different threshold concentrations of the corresponding sulfide in the reaction system. According to the data obtained, the threshold content of CuS in water exceeds that of ZnS by more than 16 times.

The formation of copper and zinc sulfides in a cysteine solution makes it possible to substantially increase the

Table 1. Mean size of the primary particles (d) in precipitates of unmodified CuS and ZnS at different concentrations of copper or zinc ions ($[M^{2+}]$) and sulfur ions ($[S^{2-}]$) in the reaction solution according to the TEM data

$[M^{2+}] = [S^{2-}]$ /mol L^{-1}	d/nm	
	CuS	ZnS
$1 \cdot 10^{-4}$	8.0±1.6	2.4±0.5
$5 \cdot 10^{-4}$	16.0±1.7	—
$1 \cdot 10^{-3}$	—	3.8±0.7

threshold concentration of the sol—precipitate transition for both CuS and ZnS. In this case, $[\mathrm{CuS}]_{\mathrm{threshold}}$ in water is $1.0 \cdot 10^{-3}$ mol L^{-1}, and that in a cysteine solution is $1.7 \cdot 10^{-2}$ mol L^{-1}, while $[\mathrm{ZnS}]_{\mathrm{threshold}}$ in water is $4.0 \cdot 10^{-4}$ mol L^{-1}, in a cysteine solution being $5.8 \cdot 10^{-3}$ mol L^{-1}, *i.e.*, increases by 17 and 14.5 times, respectively.

The data obtained made it possible to use the dynamic light scattering (DLS) method to determine sizes of the primary (non-associated into aggregates) CuS particles by the TEM-independent method and to confirm the enhanced affinity of zinc sulfide to the formation of associates compared to copper sulfide under other equal conditions. It turned out that the mean size of the unmodified primary CuS particles obtained in water under the condition that $[\mathrm{Cu}^{2+}] = [\mathrm{S}^{2-}] = 1 \cdot 10^{-4}$ mol L^{-1} is 9.6±0.4 nm, which well agrees with the data in Table 1. When the CuS particles are formed in a cysteine solution under the similar conditions, the mean size of the primary particles decreases to 5.1±0.4 nm, *i.e.*, almost twofold. The size distributions of the primary particles in water and in a cysteine solution are shown in Fig. 1.

An increase in the copper sulfide content in a modifying solution of cysteine to $[\mathrm{CuS}] = 1 \cdot 10^{-2}$ mol L^{-1} (Table 2, Fig. 2) results in some increase in the mean size of the primary CuS particles in sols resistant to aggregation during several weeks. The further increase in the CuS content decrease the aggregative stability of these systems to several days.

The influence of a modifying solution of cysteine on the particle size of ZnS was studied at $[\mathrm{Zn}^{2+}] = [\mathrm{S}^{2-}] = 1 \cdot 10^{-4}$ mol L^{-1}. The ZnS sols prepared under the conditions indicated in Table 3 were studied by the DLS method four days after preparation.

Table 2. Sizes of the primary CuS particles in a cysteine solution at different concentrations of CuS in the reaction medium according to the DLS data*

[CuS]/mol L^{-1}	d_{max}/nm	d/nm
$1.0 \cdot 10^{-3}$	4.8	5.1±0.4
$3.3 \cdot 10^{-3}$	5.6	6.3±0.4
$1.0 \cdot 10^{-2}$	6.4	6.6±0.4

* Reaction concentrations: $[\mathrm{Cu}^{2+}] = [\mathrm{S}^{2-}] = 1 \cdot 10^{-4}$ mol L^{-1}; d_{max} is the particle size at the maximum of their size distribution curve; d is the mean particle size.

A comparison of the results obtained by the TEM method (see Table 1) and the data shown in Fig. 3 and in Table 3 suggests that associates 10—30 nm in size stabilized in a cysteine solution are formed in the system studied in spite of the visual transparency of ZnS sols, which is retained for a long time. The associate size increases with an increase in the total concentration of zinc sulfide in a solution, and a precipitate begins to form when the associates achieve the size $d > 40$ nm. The mean sizes of primary particles in the ZnS associates obtained in water and in a cysteine solution at the reaction concentrations $[\mathrm{Zn}^{2+}] = [\mathrm{S}^{2-}] = 1 \cdot 10^{-3}$ mol L^{-1} were determined by the TEM method, being 3.8±0.7 and 1.5±0.2 nm, respectively. The data obtained by the TEM method were confirmed by UV spectroscopy. It is known from published data that the electromagnetic excitation of semiconductors results in the formation of a weakly bound electron—hole pair, namely, the Wannier—Mott exciton.[8] The electronic characteristics of the semiconductor begin to change with a decrease in the crystal to sizes comparable with the Bohr radius of the exciton. A striking example of these changes is the hypsochromic shift of the exciton absorption band of the crystal with a decrease in its size. Therefore, sizes of

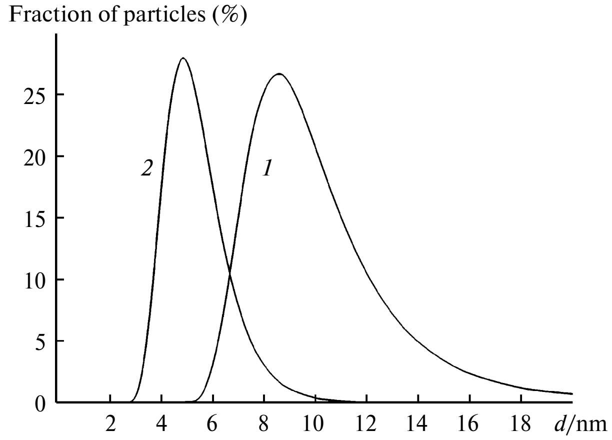

Fig. 1. Size distribution of the CuS particles unmodified (*1*) and modified with cysteine (*2*). $[\mathrm{CuS}] = 1 \cdot 10^{-3}$ mol L^{-1}, $[\mathrm{Cu}^{2+}] = [\mathrm{S}^{2-}] = 1 \cdot 10^{-4}$ mol L^{-1}.

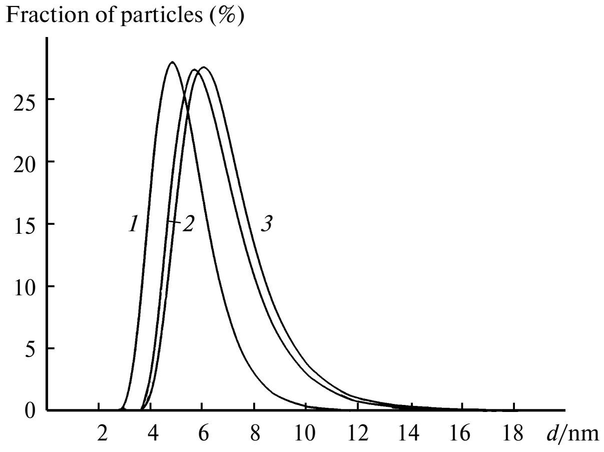

Fig. 2. Size distribution of the cysteine-modified CuS particles at different CuS concentrations in the reaction mixture: $1 \cdot 10^{-3}$ (*1*), $3.3 \cdot 10^{-3}$ (*2*), and $1 \cdot 10^{-2}$ mol L^{-1} (*3*). $[\mathrm{Cu}^{2+}] = [\mathrm{S}^{2-}] = 1 \cdot 10^{-4}$ mol L^{-1}.

Table 3. Sizes of associates of the primary ZnS particles in a cysteine solution at different ZnS concentrations in the reaction medium according to the DLS data*

[ZnS]/mol L^{-1}	d_{max}/nm	d/nm
$2.8 \cdot 10^{-3}$	11.4	11.9±0.8
$4.0 \cdot 10^{-3}$	16.5	19.0±2.3
$5.0 \cdot 10^{-3}$	22.8	25.0±2.4

* Reaction concentrations: $[Zn^{2+}] = [S^{2-}] = 1 \cdot 10^{-3}$ mol L^{-1}; d_{max} is the particle size at the maximum of their size distribution curve; d is the mean particle size.

rather fine particles can be estimated by spectral methods. For instance, it was shown[9] that the decrease in the ZnS crystal size from 4.4 to 3.3 nm induces the shift of the exciton band from 306 to 291 nm.

Figure 4 shows the UV spectra of the freshly prepared sol of unmodified ZnS (Fig. 4, curve *1*), which was obtained by fast pouring together of solutions of zinc sulfate and sodium sulfide with concentrations of 10^{-3} mol L^{-1}, and the spectrum of the cysteine-modified sol of zinc sulfide prepared by the double dropping method with the dilution of the initial solution of zinc sulfate and sodium sulfide to the reaction concentration 10^{-3} mol L^{-1} (Fig. 4, curve *2*). According to Fig. 4, the spectrum of the sol of the cysteine-modified ZnS particles has an absorption band with a maximum at 275 nm. Therefore, with allowance for the published data,[9] the size of the primary ZnS particles obtained under our conditions should be less than 3 nm. As has been shown above, according to the TEM data, this size is 1.5±0.2 nm.

The broad low-intensity absorption band of unmodified ZnS has a maximum about 290 nm (see Fig. 4, curve *1*), which corresponds, according to Ref. 9, to the size of the ZnS crystal equal to 3.3 nm, while according to our TEM data this size is 3.8 nm. Thus, the results of this work obtained by TEM and UV spectroscopy are in good agreement between each other and with literature data.

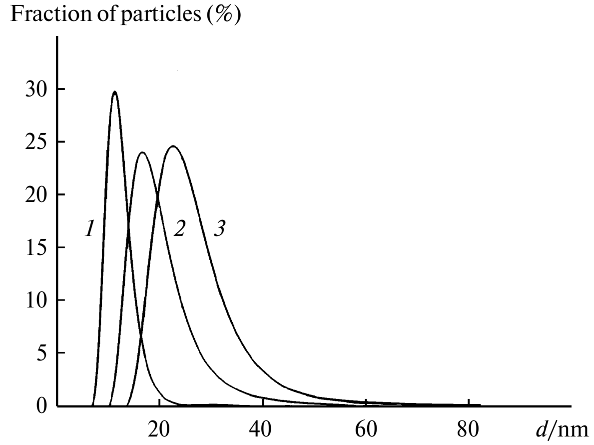

Fig. 3. Size distribution of the ZnS associates in a cysteine solution at different ZnS concentrations in the reaction mixture: $2.8 \cdot 10^{-3}$ (*1*), $4.0 \cdot 10^{-3}$ (*2*), and $5.0 \cdot 10^{-3}$ mol L^{-1} (*3*). $[Zn^{2+}] = [S^{2-}] = 1 \cdot 10^{-4}$ mol L^{-1}.

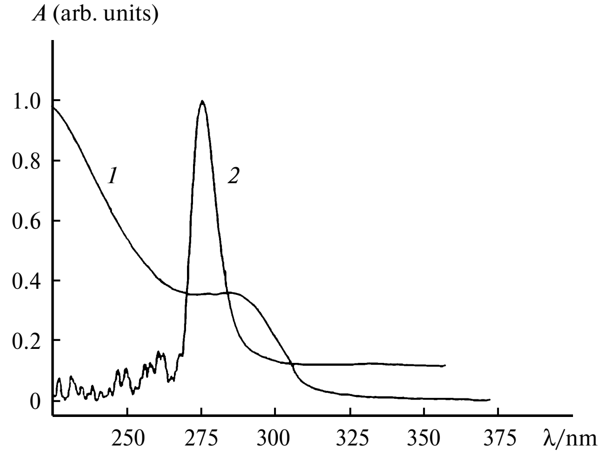

Fig. 4. UV spectra of ZnS sols in water (*1*) and in a cysteine solution (*2*). $[Zn^{2+}] = [S^{2-}] = 10^{-3}$ mol L^{-1}.

The decrease in the size of the CuS and ZnS primary particles formed in a cysteine solution compared to the particles formed in water (see Fig. 1) indicates that their growth is restricted due to the modification of the surface with cysteine molecules. This is confirmed by the elemental analysis data for carbon. For instance, the modified CuS samples contain 4.2% of carbon on the average, whereas some ZnS samples contain 10% of carbon, which corresponds to the extremely high density of grafting of the modifier to the nanocrystal surface, being several molecules per square nanometer.

The XPS spectra of unmodified CuS presented in Fig. 5, *a* contain the signal of sulfur of the sulfide group ($E_b \approx 162$ eV) and the signal of oxidized sulfur ($E_b \approx 168$ eV); the band of the copper ion has a shoulder at the right and a characteristic satellite at 940—947 eV. The spectrum of the CuS sample obtained in a cysteine solution exhibits substantial changes in the shape of the corresponding spectrum (see Fig. 5, *b*): a band characteristic of the sulfur atom of the thiol or disulfide group ($E_b = 164.5$ eV) and the intensity of the band of oxidized sulfur ($E_b = 167.5$ eV), which is present in unmodified CuS decreases considerably.

The XPS spectra of ZnS modified and unmodified with cysteine are more complicated but differ noticeably from each other, which indicates, in our opinion, as in the case of CuS, in favor of a change in the composition of the surface due to chemical modification with cysteine.

Thus, the application of the double dropping method in combination with the use of cysteine as a modifier makes it possible to obtain preparative amounts of nanoparticles of copper and zinc sulfides in homogeneous aqueous solutions. Depending on the concentration of the reactants,

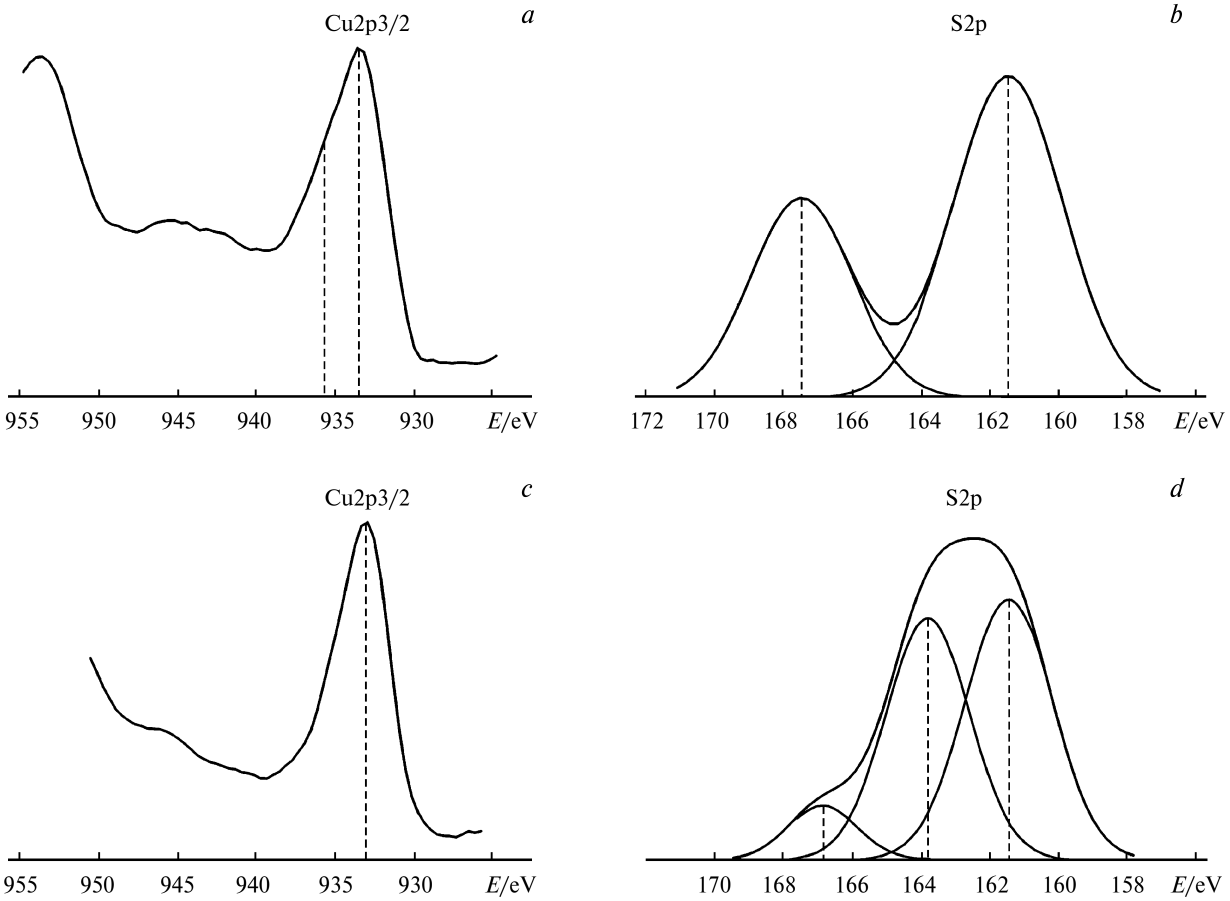

Fig. 5. X-ray photoelectron spectra of CuS unmodified (*a*, *b*) and modified with cysteine (*c*, *d*).

the size of the particles formed is 5—7 and 1.5—3 nm for copper and zinc sulfides, respectively. Sols of these nanoparticles are resistant to oxidation and coagulation within several weeks. Associates of the nanoparticles 10—30 nm in size are formed in the system with an increase in the total concentration of the sulfides, which is most pronounced for zinc sulfide. The use of cysteine makes it possible to increase the threshold concentration of the sol—precipitate transition by 15—17 times. It was established by elemental analysis and XPS that in cysteine solutions the surface of the cooper and zinc sulfide particles is modified, which prevents their further growth and substantially retards aggregation. The variation of the synthesis conditions allows one to obtain zinc sulfide particles with optical properties, which are related to size effects.

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Received March 11, 2009;
in revised form March 16, 2010