



Catalytic activity of CuS nanoparticles in hydrosulfide ions air oxidation

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Abstract

Photophysical characteristics of colloidal CuS nanoparticles synthesized in various conditions and stabilized in aqueous solutions with sodium polyphosphate (SPP) were studied. A correlation between the band gap of CuS nanoparticles and their average diameter was established.

Catalytic activity of colloidal CuS nanoparticles in sodium sulfide air oxidation in aqueous solutions at atmospheric pressure and room temperatures was established and thoroughly investigated. Kinetics of HS⁻ oxidation and the nature of principal products of this reaction (thiosulfate and sulfate ions) were elucidated. A scheme for the mechanism of hydrosulfide ions catalytic oxidation was proposed. Accordingly to the scheme, HS⁻ oxidation is a chain-radical reaction initiated on the surface of CuS nanoparticles and propagating further in the bulk of a solution.

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1. Introduction

Hydrogen sulfide and its water-soluble salts are widespread impurities of the waste waters of metallurgy, coke, shale-processing, asphalt, cellulose, food, pigments, artificial silk, leather and other industries [1–3]. In cities hydrogen sulfide is formed in substantial amounts in drainage systems at biocatalytic reduction of sulfates and through biomass decomposition.

There are many methods for hydrogen sulfide removal from the waste waters, in particular reagent and sorption water purification, bio-, electro-, photo- and radiochemical decomposition (or oxidation) of H₂S and sulfide ions, but the most efficient technique is the catalytic aeration of the waste waters, i.e. H₂S oxidation in air-saturated solutions in the presence of catalysts. Activated carbon, nature and artificial zeolites, polymeric fibers and cellular polymers, modified with transition metals ions are widely used as aeration catalysts [1–5].

In the present paper we discuss the results of the investigation of catalytic activity of nanometer colloidal copper(II) sulfide particles stabilized with sodium polyphosphate (SPP) in the oxidation of hydrosulfide ions by molecular oxygen in aqueous solutions at room temperatures and atmospheric pressure. Attempts of the interpretation of the kinetics of this process stimulated an investigation of optical characteristics of CuS nanoparticles, synthesized in various conditions, including the substitution of Cd²⁺ by Cu²⁺ ions in the lattice of CdS nanoparticles of known diameter. The data obtained in that way let us establish a correlation between the band gap of CuS nanoparticles (E_g) and their average diameter ($2R$) analogous to the well-known correlation $E_g - (2R)$ for CdS nanoparticles (see for example [6]).

It is worthy of notice that along with the plenty of papers concerning the photophysical and photochemical properties of some semiconductor nanoparticles, especially CdS, ZnO, TiO₂, WO₃ and MoS₂ [6–8], as well as their capability to catalyze various photochemical reactions [6], there are virtually no literature examples of the investigation of the properties of semiconductor nanocrystals which are not directly bound with the light absorption, in particular, their catalytic activity in redox-transformations proceeding without the irradiation. The present paper is a part of a cycle of the investigations of photophysical properties and catalytic

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activity of some metal-sulfide semiconductor nanoparticles, in particular CuS, Cu₂S and Ag₂S [9–12], which we hope could fill the above-mentioned gap.

2. Experimental

Copper(II) sulfide colloids were prepared by two different methods: (a) in a reaction between diluted aqueous solutions of CuSO₄ (reagent grade) and Na₂S (reagent grade, Aldrich) in the presence of a stabilizer—sodium polyphosphate (NaPO₃)_{*n*} (reagent grade, Aldrich) at intense stirring; (b) through the complete substitution of Cd²⁺ cations with Cu²⁺ in CdS nanoparticles obtained by mixing of diluted aqueous solutions of Cd(CH₃COO)₂ (reagent grade) and Na₂S in the presence of SPP [13]. Sodium sulfide solutions were prepared immediately before the synthesis of CdS and CuS in distilled water bubbled with argon. Electronic absorption spectra were recorded with the use of Specord UV-Vis spectrophotometer.

Concentrations of sulfur-containing species (HS⁻, SO₄²⁻, SO₃²⁻, S₂O₃²⁻) in solutions were determined spectrophotometrically using correspondingly (a) methylene blue dye formation ($\lambda_{\max} = 670$ nm, $\varepsilon_{670} = 24600$ M⁻¹ cm⁻¹) in the reaction between H₂S and *N,N*-dimethyl-*n*-phenylenediamine in the presence of Fe(III) in strong-acid media [14]; (b) free chloranilic acid ($\lambda_{\max} = 320$ nm) generation in the reaction of SO₄²⁻ with an excess of barium chloranilate [15]; (c) formation of a dye ($\lambda_{\max} = 590$ nm) in a reaction between SO₃²⁻ and fuchsine in the presence of formaldehyde in water–alcohol mixtures [15]; (d) reduction of I₃⁻ complex ($\lambda_{\max} = 360$ nm, $\varepsilon_{360} = 24000$ M⁻¹ cm⁻¹) by S(II–IV) compounds resulting in a decrease in the optical density of I₃⁻ solution [14]. S₂O₃²⁻ concentrations were calculated by the subtraction of S²⁻ and SO₃²⁻ concentrations, which were determined independently, from the total S(II–IV) content.

Kinetic regularities of Na₂S photocatalytic air oxidation were studied with the use of thermostatically controlled 10.0 ml glass reactor where oxygen, air or mixture of oxygen and argon were bubbled with constant rate through a peristaltic pump. Reacting mixtures were stirred with magnetic stirrer. Diminution of HS⁻ concentration after 60 s of gas bubbling (V_{60} , M s⁻¹) was used as hydrosulfide ions oxidation rate unit.

3. Results and discussion

3.1. Synthesis and photophysical properties of CuS nanoparticles stabilized in aqueous solutions with sodium polyphosphate

It was established that the interaction between equimolar amounts of CuSO₄ and Na₂S in aqueous solutions (1×10^{-4} to 5×10^{-3} M) in the presence of SPP (5×10^{-4}

to 6×10^{-3} M) at 0–25 °C (method (a)) leads to the formation of CuS sols which are stable to aggregation. The colloids absorb the light with $\lambda < 700$ nm as a result of indirect interband transitions in copper(II) sulfide nanoparticles (see Fig. 1a), which is confirmed by the linearity of spectral curves in $(\alpha E_{hv})^{0.5} - E_{hv}$ coordinates (see Fig. 1b) [9], where E_{hv} is quantum energy (eV), $\alpha(\lambda) = 2.303 \times 10^3 D(\lambda) \rho C^{-1} d^{-1}$ the CuS absorption coefficient on the wave length corresponding to the energy E_{hv} (cm⁻¹), $D(\lambda)$ the optical density of colloidal CuS solution, ρ the density of colloidal CuS nanoparticles which was adopted to be equal to the density of bulk covellite (4.6 g cm⁻³) [16], C the CuS concentration (g cm⁻³), d the optical path. Extrapolation of a linear section of the spectral curve plotted in coordinates $(\alpha E_{hv})^{0.5} - E_{hv}$ down to the axis of abscissae let us determine the minimal energy of indirect interband transition in CuS nanoparticles $E_g + E_f$ (where E_g is the band gap of CuS nanoparticles, E_f is phonon energy [8,9,17]). Taking into account small values of E_f in semiconductors ($E_f \sim 10^{-2}$ eV [9,17]), we adopted $E_g + E_f \approx E_g$.

It is known [6–8] that one of the quantum confinement effects in ultrasmall semiconductor crystals lies in a change in their electronic characteristics (band gap width and allowed bands positions) with a change of particles dimensions in the 1–10 nm region. We established that for a number of CuS colloids synthesized by method (b) through the substitution of Cd²⁺ with Cu²⁺ in CdS nanoparticles, one can observe a distinct dependence of E_g on the average nanoparticles diameter, $2R$ (see Fig. 1c). X-axis of the correlation given in Fig. 1c corresponds to the average diameter of original CdS nanoparticles, whereas Y-axis corresponds to E_g values of the resulting CuS nanoparticles. When calculating the correlation given in Fig. 1c we suggested that no substantial change of nanoparticles diameter occurs during the transformation of CdS into CuS. Such assumption is, in our opinion, quite justified, since in the course of the substitution of cadmium(II) by copper(II) the sulfur sublattice of nanocrystals remains practically undisturbed, so the average particle size should remain unchanged. It is known that the average diameter of CdS nanoparticles remains unchanged also at the complete Cd²⁺ substitution by other metals cations, for example Pb²⁺, even in spite of the difference between crystal structures of the original CdS nanoparticles (blende structure) and the resulting PbS nanoparticles (rock-salt structure) [18]. The average radii of CdS nanoparticles used for the preparation of CuS nanoparticles, were determined using equation (I) [8,13]:

$$\Delta E_g = \frac{\hbar^2 \pi^2}{(2R)^2} ((m_e^*)^{-1} + (m_h^*)^{-1})$$

where ΔE_g is a gap between E_g values of nanoparticles and bulk crystal of cadmium sulfide, \hbar the reduced Planck constant, m_e^* and m_h^* are the effective masses of CdS conduction band electrons and valence band holes, respectively.

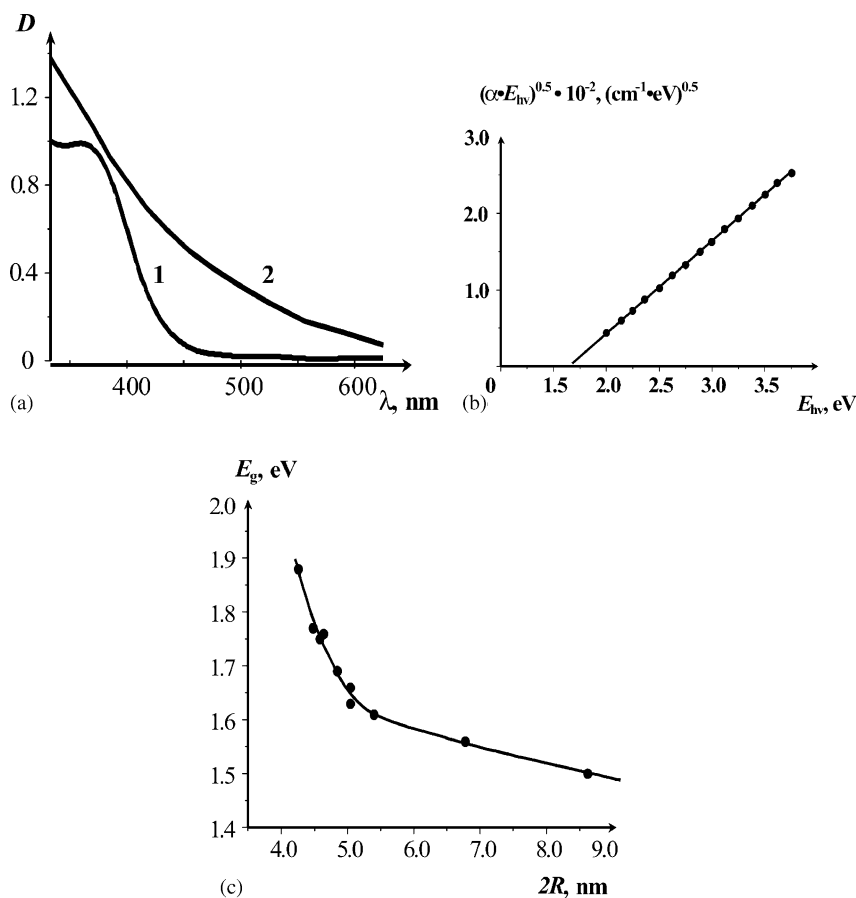


Fig. 1. (a) Electronic absorption spectra of colloidal CdS solution stabilized with sodium polyphosphate (SPP) (1) and CuS colloid obtained from CdS after the complete substitution of Cd^{2+} with Cu^{2+} (2). $[\text{CdS}] = 5 \times 10^{-4} \text{ M}$, $[\text{CuS}] = 5 \times 10^{-4} \text{ M}$, $[\text{SPP}] = 5 \times 10^{-3} \text{ M}$, optical path $d = 1 \text{ cm}$. (b) Linearization of the absorption spectrum of CuS colloid synthesized at 18°C and stabilized with SPP in coordinates $(\alpha E_{hv})^{0.5} - E_{hv}$. $[\text{CuS}] = 5 \times 10^{-4} \text{ M}$, $[\text{SPP}] = 5 \times 10^{-3} \text{ M}$. (c) Correlation between the band gap of colloidal CuS nanoparticles, synthesized from CdS (E_g) and the average diameter of parental CdS nanoparticles ($2R$).

It should be noted that since we did not accomplish any direct determination of the average size of CuS nanoparticles of different size, the correlation $E_g(R)$ can be used only for evaluation of CuS nanoparticles diameter. Fig. 1c shows that an increase in electronic transition energy induced by spatial exciton confinement [6,8] becomes especially noticeable for copper(II) sulfide particles with $2R < 5 \text{ nm}$. Using the correlation given in Fig. 1c we established that the average diameter of CuS nanoparticles synthesized by method (b) and used as catalysts of HS^- oxidation, did not exceed 10 nm.

As can be seen from the data given in Table 1, variations in the reagents and stabilizer concentrations, as well as in temperature and pH at which the synthesis of CuS colloid is performed, allow to obtain purposefully CuS nanoparticles with certain band gap (from 1.25 to 1.75 eV) and the average diameter (from $2R \geq 5 \text{ nm}$).

Air bubbling through CuS colloids results in a decrease in the intensity of the absorption band of a solution. Since the absorption band of CuS colloid restores to the initial form after an addition of some excess of sodium sulfide, so such behaviour of a solution was connected with the partial oxidation of CuS particles by dissolved oxygen. Such reactivity

of CuS nanoparticles towards O_2 molecules determines apparently their high catalytic activity in hydrosulfide ions air oxidation.

3.2. Catalytic activity of CuS nanoparticles in HS^- oxidation by molecular oxygen

Hydrosulfide ions air oxidation in aqueous solutions at room temperatures and atmospheric pressure proceeds with small rates in the absence of catalysis and increases substantially upon the injection of CuS nanoparticles into a reacting mixture (see Fig. 2 and Table 2, row 1). To establish possible mechanism of HS^- catalytic oxidation we performed detailed investigation of the kinetics of this reaction and studied dependences of oxidation rates on reagents concentrations, temperature and pH of the medium and determined also composition of a mixture of HS^- oxidation products. It was found that the rate of HS^- catalytic oxidation grows at an increase in molar CuS concentration (see Table 2, row 1), initial concentration of Na_2S (see Table 2, row 2), volume fraction of oxygen in gas mixture bubbled into the reactor (see Table 2, row 3) as well as pH of a solution—up to 11.9

Table 1
Dependence of E_g of colloidal CuS particles upon the synthesis conditions

No.	[CuS] × 10 ⁴ (M)	[SPP] × 10 ³ (M)	[Na ₂ S] × 10 ³ (M)	pH	T·(°C)	E_g ·(eV)
1	2.0	5.0	–	6.5	18	1.69
	5.0	5.0	–	6.5	18	1.58
	10.0	5.0	–	6.5	18	1.54
	20.0	5.0	–	6.5	18	1.38
2	1.0	5.0	10.0	11.9	18	1.75
	2.0	5.0	10.0	11.9	18	1.60
	5.0	5.0	10.0	11.9	18	1.53
	10.0	5.0	10.0	11.8	18	1.44
	20.0	5.0	10.0	11.8	18	1.40
3	2.0	5.0	–	6.8	3–5	1.72
	2.0	5.0	–	6.8	10	1.69
	2.0	5.0	–	6.8	25	1.66
	2.0	5.0	–	6.8	70	1.56
4	2.0	5.0	0.5	–	18	1.58
	2.0	5.0	1.0	–	18	1.58
	2.0	5.0	5.0	–	18	1.50
5	5.0	0	–	6.8	18	1.41
	5.0	0.5	–	6.8	18	1.69
	5.0	1.0	–	6.8	18	1.71
	5.0	2.0	–	6.8	18	1.75
	5.0	6.0	–	7.2	18	1.75
6	5.0	5.0	–	11.6	18	1.70
	5.0	5.0	–	6.5	18	1.69
	5.0	5.0	–	4.8	18	1.70
	5.0	5.0	–	3.5	18	1.63

(see Table 2, row 4). Linearization of these dependences in logarithmic coordinates enabled us to calculate kinetic orders of HS[−] oxidation on CuS, Na₂S, O₂ and HO[−] concentrations, which proved to be equal to 0.5, 1.0, 0.7 and

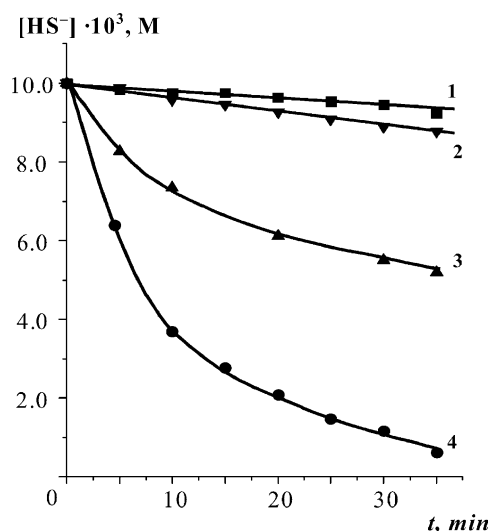


Fig. 2. Change in sodium sulfide concentration in a solution due to HS[−] oxidation by air in the absence of catalysts (1), in the absence of catalysts by pure oxygen (2), by air in the presence of CuS nanoparticles (3), by pure oxygen in the presence of CuS nanoparticles (4). [CuS] = 1 × 10^{−3} M; [SPP] = 5 × 10^{−3} M; gas mixture bubbling rate, 100 ml min^{−1}; reactor volume, 10 ml.

Table 2
Rates of hydrosulfide ions air oxidation in various conditions

No.	[CuS] × 10 ⁴ (M)	[Na ₂ S] × 10 ³ (M)	ν(O ₂) (%)	pH	T·(°C)	V × 10 ⁴ (M min ^{−1})	
1	0	10.0	19	11.9	18	0.25	
	2.0	10.0	19	11.9	18	0.70	
	3.5	10.0	19	11.9	18	1.20	
	5.0	10.0	19	11.9	18	1.40	
	6.0	10.0	19	11.9	18	1.65	
	8.0	10.0	19	11.9	18	1.80	
	10.0	10.0	19	11.9	18	2.05	
	12.5	10.0	19	11.9	18	2.10	
	2	5.0	2.0	19	10.2	18	0.35
		5.0	4.0	19	10.6	18	0.50
5.0		6.5	19	11.2	18	0.90	
5.0		8.0	19	11.7	18	1.15	
5.0		10.0	19	11.9	18	1.40	
5.0		12.0	19	12.1	18	1.50	
3	5.0	16.0	19	12.6	18	2.10	
	10.0	12.0	19	12.1	20	2.20	
	10.0	12.0	36	12.1	20	4.40	
	10.0	12.0	60	12.1	20	5.20	
	10.0	12.0	84	12.1	20	7.70	
4	5.0	12.0	19	10.2	18	0.25	
	5.0	12.0	19	11.2	18	0.95	
	5.0	12.0	19	11.5	18	1.40	
	5.0	12.0	19	11.7	18	1.60	
	5.0	12.0	19	11.9	18	1.70	
	5.0	12.0	19	12.2	18	1.35	
	5.0	12.0	19	12.8	18	0.40	
	5	0	12.0	19	12.1	16	0.20
		0	12.0	19	12.1	30	0.30
		0	12.0	19	12.1	50	0.60
5.0		12.0	19	12.1	16	1.60	
5.0		12.0	19	12.1	30	1.35	
5.0		12.0	19	12.1	50	1.10	

Note: The rate of gas bubbling, 100 ml min^{−1}; reactor volume, 10 ml.

0.5 correspondingly. An increase in the rate of catalytic oxidation at the increase of pH of reacting mixture up to 11.9 may be connected with the participation of hydroxide ions in certain steps of this complex process, while a decrease in the oxidation rate observed at higher pH (see Table 2, row 4) may be explained, in our opinion, by the competition between HS[−] and HO[−] anions for adsorption sites on the surface of CuS nanoparticles in strong-alkaline media.

An increase in the temperature of a reacting mixture exerts contrariwise influence upon the rates of heterogeneous catalytic and homogeneous non-catalytic oxidation of sodium sulfide. Thus, HS[−] oxidation rate in the presence of CuS nanoparticles decreases at an increase in temperature of a solution, while usual Arrhenius dependence of the oxidation rate on the temperature is observed in the absence of catalysts (see Table 2, row 5). The study on the influence of the temperature on optical properties of CuS colloids allowed us to suppose at least two different reasons for a reduction in the catalytic activity of CuS nanoparticles at an increase in the temperature of a reacting mixture. The first reason lies in the agglomeration of CuS particles upon heating of

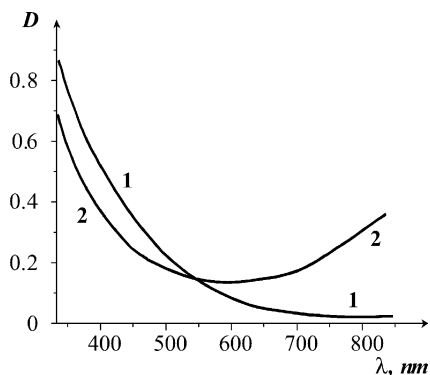


Fig. 3. Electronic absorption spectra of colloidal CuS solution synthesized at 18 °C (1), and heated for 15 min at 70 °C (2). $[\text{CuS}] = 5 \times 10^{-4} \text{ M}$, $[\text{SPP}] = 5 \times 10^{-3} \text{ M}$.

the colloidal solution, which is indicated by a decrease in E_g value (and subsequently in the average diameter of CuS nanoparticles) at the synthesis or post-synthesis ageing of a colloid at raised temperatures. The second reason consists, in our opinion, in an alteration of the state of the surface of CuS nanoparticles upon heating of a colloidal solution. An increase in the temperature at the synthesis of CuS nanoparticles as well as heating of already formed colloidal particles in aerobic conditions leads to the evolution of a new absorption band with a maximum lying in near infra-red region of the spectrum at $\lambda \sim 1200 \text{ nm}$ (see Fig. 3) [9]. In literature one can find different interpretations of the nature of spectral changes observed in the near-IR section of the spectra of CuS colloids [8,9,19–21]. The most probable reason for the evolution of the IR-band is, in our opinion, formation of copper(I, II) oxides layer on the surface of CuS nanoparticles and generation of chromophoric centers within this layer, which are analogous to polynuclear mixed-valence copper(I, II) complexes with oxygen-containing ligands having similar intervalence charge transfer absorption bands in near IR spectral region [20,21]. Transformation of a surface layer of CuS nano-particles which essentially mediates HS^- oxidation should, as we suppose, hamper adsorption of hydrosulfide ions from the bulk of a solution and inhibit subsequent electron transfer with the participation of CuS valence band holes and adsorbed HS^- ions.

It should be noted that colloidal CuS nanoparticles retain its catalytic activity in the consecutive oxidation of several (at least four) portions of Na_2S centimolar solutions. Spectral properties of CuS nanoparticles characterizing their size and surface state (intensity and edge of the fundamental adsorption band, E_g values) remain unchanged at multifold utilization of colloidal solution.

Analysis of reacting mixtures performed in the course of HS^- catalytic oxidation showed that the main products of the reaction are thiosulfate and sulfate ions (see Fig. 4). At initial stages of the process small amounts of polysulfides are permanently present in solution. Accumulation of polysulfides is accompanied by the evolution of an absorption band with maximum at 360–370 nm, which is characteristic

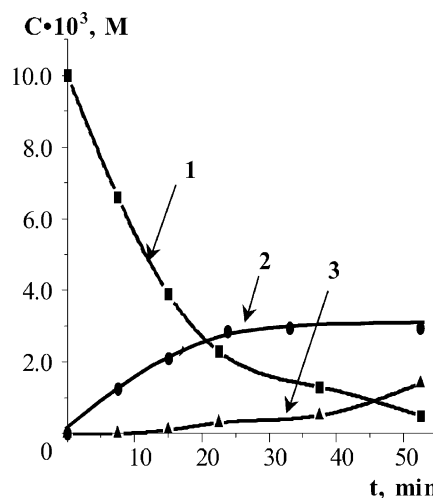


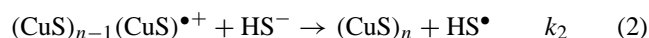
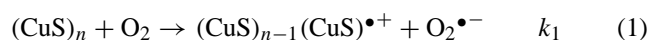
Fig. 4. HS^- concentration decrease (1) and simultaneous accumulation of the oxidation products: SO_3^{2-} (2) and SO_4^{2-} (3) in a solution containing $[\text{CuS}] = 5 \times 10^{-4} \text{ M}$, $[\text{Na}_2\text{S}] = 1 \times 10^{-2} \text{ M}$, $[\text{SPP}] = 5 \times 10^{-3} \text{ M}$. Air bubbling rate, 100 ml min^{-1} ; reactor volume, 10 ml.

for S_x^{2-} (where $x = 2-4$) in aqueous solutions at room temperatures [22]. Formation of sulfite ions in the course of HS^- oxidation was not observed.

3.3. A scheme for a mechanism of hydrosulfide ions air oxidation in the presence of CuS nanoparticles

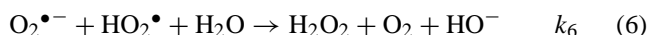
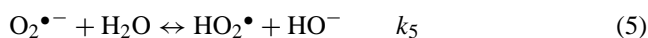
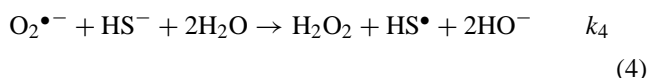
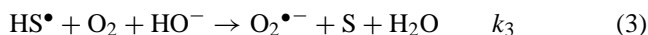
It is known that hydrosulfide ions oxidation in aqueous solutions at room temperatures in the absence of catalysts is a chain-radical process [1–3,23–25]. HS^\bullet and $\text{O}_2^{\bullet-}$ radicals forming in the chain initiation stage at the interaction of oxygen molecules with HS^- ions, are the primary intermediates responsible for the propagation of chain oxidation. The process of initiation has small rate ($k = 1.5 \times 10^{-3} \text{ M}^{-1} \text{ s}$ [25]) in the absence of catalysts and determines apparently the overall rate of homogeneous hydrosulfide oxidation.

Copper(II) sulfide is a degenerated p-type semiconductor with Fermi level lying within the valence band [19]. Conductivity of CuS in ground state is therefore determined by delocalized holes, which are able to oxidize adsorbed substrates. At the same time a decrease in the intensity of the absorption band of colloidal CuS upon air bubbling in the absence of an excess of Na_2S indicates the possibility of CuS nanoparticles oxidation by molecular oxygen. In the presence of excessive hydrosulfide ions the intensity of the absorption band of colloidal CuS remains unchanged at prolonged air bubbling, thus indicating the stabilizing role of HS^- ions in the oxidation of colloidal CuS [19,26]. Taking into account the above-stated considerations, the initiation of hydrosulfide ions oxidation on the surface of CuS nanoparticles may be described by the following reactions:

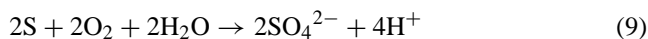
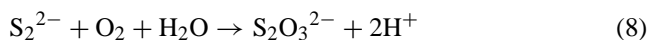
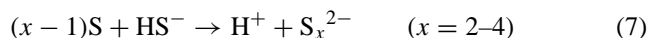


Unfortunately we could not find the values of k_1 and k_2 in literature sources. Available data, in particular [26], where an investigation of the interaction of CuFeS₂ nanoparticles with one-electron oxidants both in the absence and in the presence of HS⁻ excess was accomplished and the values of k_1 and k_2 were shown to be as high as $10^7 \text{ M}^{-1} \text{ s}$, indicate indirectly that reactions (1) and (2) do have sufficiently high rates.

The propagation of chain oxidation takes place in the bulk of a solution with the participation of HS[•] and O₂^{•-} radicals forming in the stages (1) and (2):



In the foregoing scheme, the stages (1) and (2) describe the initiation of chain-radical HS⁻ oxidation on the surface of copper(II) sulfide nanoparticles, reactions (3) and (4) correspond to the propagation of chain HS⁻ oxidation in the bulk of a solution, reaction (6) is the principal chain termination route [23,25]. Oxidation products (S_x²⁻, S₂O₃²⁻ and SO₄²⁻) accumulate in the following reactions:



An analysis of the aforecited scheme leads to the following expression for the rate of sodium sulfide air oxidation in the presence of CuS nanoparticles:

$$-\frac{d[\text{HS}^-]}{dt} = k_2[\text{CuS}][\text{HS}^-] + k_4[\text{HS}^-][\text{O}_2^{\bullet-}] \quad (\text{I})$$

Using an approximation of stationary concentrations we obtain the following expressions:

$$-\frac{d[\text{O}_2^{\bullet-}]}{dt} = k_1[\text{CuS}][\text{O}_2] + k_3[\text{HS}^\bullet][\text{O}_2][\text{HO}^-] - k_4[\text{O}_2^{\bullet-}][\text{HS}^-] - k_6[\text{O}_2^{\bullet-}][\text{HO}_2^\bullet] = 0 \quad (\text{II})$$

$$-\frac{d[\text{HS}^\bullet]}{dt} = k_2[\text{CuS}^\bullet][\text{HS}^-] + k_4[\text{O}_2^{\bullet-}][\text{HS}^-] - k_3[\text{HS}^\bullet][\text{O}_2][\text{HO}^-] = 0 \quad (\text{III})$$

Solution of the equations (I)–(III) with the assumption of sufficiently long oxidation chains (when we may neglect the initiation rate in comparison with the contribution of reactions (4) and (5) in the overall HS⁻ oxidation rate),

analogously to [23], gives us final expression for the HS⁻ catalytic oxidation rate:

$$-\frac{d[\text{HS}^-]}{dt} = \frac{k_1 k_4}{\sqrt{k_5 k_6}} [\text{HS}^-] \sqrt{[\text{CuS}][\text{O}_2][\text{HO}^-]} \quad (\text{IV})$$

Exponents values at CuS, HS⁻, O₂, HO⁻ concentrations in equation (IV), equal to 0.5, 1.0, 0.5, 0.5, well coincide with corresponding experimental values of kinetic orders of hydrosulfide ions air oxidation catalyzed by CuS nanoparticles. So, the proposed scheme for the mechanism of the process under investigation reflects adequately all observed kinetic regularities, although the lack of the values of rate constants of the initiation stage (reactions 1 and 2) do not allow us to use expression (IV) for direct calculation of the rates of catalytic HS⁻ air oxidation in various conditions. Accordance of the scheme of HS⁻ chain-radical air oxidation with experimental results indicate also that CuS nanoparticles play in this process principally the role of initiators and do not affect appreciably the propagation of chain oxidation in the bulk of a solution. However, in contrast to “classical” initiators, which are usually consumed in the course of initiation, in solutions, containing sufficiently high amounts of hydrosulfide ions, CuS nanoparticles do not undergo any changes during oxidation, i.e. they display the features of true catalyst.

4. Conclusions

In the paper we discussed the results of the investigation of photophysical characteristics of colloidal CuS nanoparticles stabilized in aqueous solutions with sodium polyphosphate and synthesized in various conditions, including the substitution of Cd²⁺ by Cu²⁺ in CdS nanoparticles of known average diameter. The study of optical properties of CuS particles synthesized from CdS nanocrystals of various average size allowed us to establish a correlation between the band gap of CuS nanoparticles and their average diameter.

Catalytic activity of colloidal CuS nanoparticles in the hydrosulfide air oxidation in aqueous solutions at atmospheric pressure and room temperatures was established and thoroughly investigated. We studied in details kinetics of the oxidation and found that the principal products of this reaction are thiosulfate and sulfate ions. We proposed a scheme for the mechanism of hydrosulfide ions catalytic oxidation. Accordingly to the scheme, HS⁻ oxidation is a chain-radical reaction initiated on the surface of CuS nanoparticles and propagated further in the bulk of a solution.

References

- [1] G.A. Zakhalyavko, N.V. Gorokhovatskaya, V.V. Goncharuk, Chem. Technol. Water 8 (1986) 21 (in Russian).
- [2] G.A. Zakhalyavko, N.V. Gorokhovatskaya, V.V. Goncharuk, Chem. Technol. Water 9 (1987) 459.

- [3] G.A. Zakhalyavko, S.S. Stavisskaya, I.A. Tarkovskaya, N.V. Gorokhovatskaya, V.V. Goncharuk, Chem. Technol. Water 11 (1989) 982.
- [4] T.V. Min, V.P. Stoyan, A.P. Rudenko, Zhurn. Fiz. Chim. 69 (1995) 2241 (in Russian).
- [5] G.I. Emelyanova, L.E. Gorlenko, L.V. Voronova, M.P. Zverev, V.V. Lunin, Kinetics Catal. 40 (1999) 90.
- [6] J.Z. Zhang, J. Phys. Chem. B 104 (2000) 7239.
- [7] D.W. Bahnemann, Isr. J. Chem. 33 (1993) 115.
- [8] R.F. Khairutdinov, Uspekhi Khimii 67 (1998) 125 (in Russian).
- [9] A.I. Kryukov, S.Ya. Kuchmii, A.V. Korzhak, N.N. Zinchuk, A.E. Raevskaya, A.L. Stroyuk, Theor. Exp. Chem. 35 (1999) 92 (in English).
- [10] S.Ya. Kuchmiji, A.V. Korzhak, A.E. Raevskaya, A.I. Kryukov, Theor. Exp. Chem. 37 (2001) 31.
- [11] A.I. Kryukov, N.N. Zinchuk, A.V. Korzhak, S.Ya. Kuchmii, Theor. Exp. Chem. 37 (2001) 352.
- [12] A.I. Kryukov, N.N. Zinchuk, A.V. Korzhak, S.Ya. Kuchmii, Theor. Exp. Chem. 39 (2003) 8.
- [13] A.E. Raevskaya, A.L. Stroyuk, S.Ya. Kuchmii, Theor. Exp. Chem. 39 (2003) 153.
- [14] G. Charlot, Les Methodes de la Chimie Analytique, Analyse Quantitative Minérale, Masson Ed., Paris, 1961.
- [15] Z. Holzbecher, L. Diviš, L. Šůcha, F. Vláčil, Organická ěinidla v Anorganické Analýze, SNTL, Praha, 1975.
- [16] H. Remy, Lehrbuch der Anorganischen Chemie, Band II, Leipzig, 1960.
- [17] V.I. Fistul, Introduction to Semiconductor Physics (Russian), Moscow, Vysshaya Shkola, 1984.
- [18] H.S. Zhou, I. Honma, H. Komiyama, J.W. Haus, J. Phys. Chem. 97 (1993) 895.
- [19] K.M. Drummond, F. Grieser, T.W. Healy, E.J. Silvester, M. Giersig, Langmuir 15 (1999) 6637.
- [20] D.V. Sviridov, Thesis for a Doctor's Degree, Minsk, 1999.
- [21] R.R. Gagne, C.A. Koval, T.J. Smith, M.C. Cimolino, J. Am. Chem. Soc. 101 (1979) 4571.
- [22] S. Licht, G. Hodes, J. Manassen, Inorg. Chem. 25 (1986) 2485.
- [23] P. Resch, R.J. Field, F.W. Schneider, J. Phys. Chem. 93 (1989) 2783.
- [24] G. Rabai, M. Orban, I.R. Epstein, J. Phys. Chem. 96 (1992) 5414.
- [25] Y.-X. Zhang, R.J. Field, J. Phys. Chem. 95 (1991) 723.
- [26] E.J. Silvester, F. Grieser, D. Meisel, T.W. Healy, J.C. Sullivan, J. Phys. Chem. 96 (1992) 4382.