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Preparation of Stable Colloidal Solution of Cadmium Sulfide CdS Using Ethylenediaminetetraacetic Acid

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Abstract—By the method of chemical condensation a stable aqueous colloidal solution of nanoparticles of cadmium sulfide was obtained. The solution obtained in the daylight had a bright lemon-yellow color. For the temporary stabilization of the solution was used an organic complexone, disodium ethylenediaminetetraacetate (EDTA), that prevented coagulation of colloidal particles up to several months at 4°C. At room temperature, the solution remained stable during a month. The structure and properties of the disperse phase were studied by the X-ray diffraction, optical fluorescence, and electron microscopy. The solid particles size is about 3 nm, they have a disordered close-packed structure with the space group P6mm and possess the photoluminescence color from green to orange depending on the duration of keeping the solution. The size of coagulates was 10 nm, 100 nm, and 1 μm after keeping for 1, 2, and 4 months, respectively.

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Semiconductor nanocrystals are widely used in micro- and nanoelectronics [1]. On the basis of these structures ultra-sharp color displays are planned to create and night-vision devices of high resolution, the high-speed processors, and light emitting diodes (LED) [2]. Recent studies have shown that NADH-modified CdSe/ZnS nanoparticles (NADH is reduced form of nicotinamide adenine dinucleotide NAD^+) are excellent optical tags for efficient detection of hexogen (RDX). The lower limit of detection of explosives in this case was 10^{-10} M, which, according to [3], is much better than with other known methods.

The promising use of nanoparticles of chalcogenides of heavy metals in medicine in the methods of clinical diagnostics [4] for the early detection of cancer, tuberculosis, cardiopathy, and other diseases is based on the brightness of their fluorescence [5]. For example, diagnosis of cancer at early stages of disease development can be done precisely using fluorescent nanocrystals for labeling, visualization (passive or active) and the subsequent diagnosis of tumors. The passive visualization process is based on the ability of tumors to grow additional blood vessels, the system of these vessels is very porous and branched, that allows it to accumulate the nanocrystals. But the more effective way is the active visualization i.e. based on the capability of nanocrystals to chemical binding with biological molecules like antibodies, peptides, proteins or DNA [6–8]. These complexes can be designed so that they can detect other molecules, typical of the surface of cancer cells. In ophthalmology the semiconductor nanocrystals are used not only for the purposes of visualization [9], but also for drug delivery to the tissues of the eye, including retina and cornea [10]. Also, quantum dots are increasingly used in biology in the study of cells [11]. Thus, the living cell visualization technologies are developed. By an example of Ehrlich ascites carcinoma cells it was shown [11] that CdS/ZnS nanoparticles are able to penetrate through the cell membrane and be introduced into the cells. The degree of their luminescence depends on the physiological state of the cell, concentration and contact time of the cell with the nanoparticles.

The methods of synthesis of semiconductor nanocrystals were developed a long time ago. Currently, one of the most widely used methods is the organometallic synthesis [6, 12, 13], which resulted in the formation of monodisperse nanocrystals with a high fluorescence yield. However, the synthesized nanocrystals coated with a layer of trialkylphosphine form

stable sols only in organic solvents (chloroform, toluene, heptane, etc.). Their use in biological environments requires changing surface properties, forming on the surface hydrophilic groups. To date was published many papers on the methods of transfer of nanocrystals into the aqueous phase, a review is presented in [14]. The solubilization of nanocrystals requires additional technological operations complicating the process of synthesis. A method providing preparation of semiconductor nanoparticles directly in aqueous solution is the chemical deposition [15, 16]. However, obtaining by this method of isolated, non-agglomerated nanoparticles, i.e., stable colloidal solution, failed. In this paper we experimentally demonstrated the possibility of obtaining a stable aqueous colloidal solution of cadmium sulfide CdS in one stage using the disodium ethylenediaminetetraacetate (EDTA).

For the preparation of a colloidal solution of cadmium sulfide by chemical condensation three substances were taken: sodium sulfide Na_2S, cadmium chloride $CdCl_2$, and EDTA disodium salt $C_{10}H_{14}N_2O_8Na_2$ (Na_2H_2Y). Since all three substances are readily soluble in water, the first step consisted in the obtaining solutions of strong electrolytes. As a result of the phenomenon of hydration, i.e., interaction of ions with surrounding water molecules, all the ions in electrolyte solutions become hydrated. Thus, a solution of sodium sulfide is composed of water molecules, hydrated sodium ions, and hydrated sulfide ions: H_2O, Na^+_{aq}, S^{2-}_{aq}. Another solution, a solution of cadmium chloride, consists of water molecules, hydrated cadmium ions and hydrated chloride ions: H_2O, Cd^{2+}_{aq}, Cl^-_{aq}. The third solution, solution of disodium EDTA, is composed of water molecules, hydrated sodium ions and doubly charged ion ethylenediaminetetraacetic acid: H_2O, Na^-_{aq}, $H_2Y^{2-}_{aq}$.

At mixing these solutions to obtain the resulting solution, two reactions occur:

$$Cd^{2+}_{aq} + H_2Y^{2-}_{aq} = CdY^{2-}_{aq} + 2H^+_{aq}, \quad (1)$$

$$CdY^{2-}_{aq} + S^{2-}_{aq} = CdS\downarrow + Y^{4-}_{aq}. \quad (2)$$

Since at the preparation of cadmium sulfide all solutions had the same concentration and were taken in strictly stoichiometric amounts, the total molecular equation of the formation of the disperse phase of CdS colloidal solution can be written as

$$CdCl_2 + Na_2S = CdS\downarrow + 2NaCl. \quad (3)$$

It is known that the basic property of disperse systems is their thermodynamic nonequilibrium associated with high surface energy of the developed interphase surface. Therefore, in these systems with the particles of the dispersed phase the process of "sticking occurs," i.e., coagulation, which is observed at the mixing two solutions in stoichiometric amounts, cadmium chloride and sodium sulfide, in keeping with reaction (3). To prevent coagulation, i.e., to impart aggregative stability to the colloidal solution, as well as sedimentation stability, on the surface of solid particles should be created protective double ionic layers and the adsorption-solvate layers. These layers cause the electrostatic repulsion and prevent "adhesion" of the particles.

In this work, the preparation of aggregation- and sedimentation-stable colloidal solution is implemented by the reactions (1)–(3). When the reaction (3) proceeds, the CdS crystals are formed in a solution containing hydrated ions Na^+_{aq}, H^+_{aq}, Y^{4-}_{aq}, Cl^-_{aq}. Since solutions of $CdCl_2$ and Na_2S were taken in stoichiometric quantities, the ions of Cd^{2+}_{aq} and S^{2-}_{aq} in solution are absent. According to the classical rule of adsorption, these ions are adsorbed on the crystal that form difficultly soluble compound with the ions of the crystal, as well as the ions capable of finishing the construction of the crystal lattice of the solid phase. In the discussed solution these ions are absent. Nevertheless, the resulting colloidal solution was stable.

The stability of the solution originates from the fact that the ions Na^+, H^+, Cl^- cannot firmly adhere to the crystal surface, while the ions Y^{4-} can form with the Cd^{2+} ions belonging to the crystal surface a solid complex CdY^{2-}. Thus, the ions Y^{4-} are adsorbed on the CdS crystal, providing it with an excess negative charge. Both aggregate and sedimentation stability of the colloidal solution is achieved through the formation of double ion and the adsorption-solvate layers at the adsorption of ions Y^{4-} on the surface of the CdS disperse phase. Presumably, the formula of the micelle can be written as follows:

$$\{[CdS]_m nY^{4-}(2n-x)Na^+ \cdot (2n-x)H^+\}^{2x-} xNa^+_{aq} xH^+_{aq}.$$

EXPERIMENTAL

X-ray diffraction analysis of the CdS disperse phase. The X-ray diffraction was registered on a diffractometer DRON-UM by the method of Bragg-Brentano. The X-ray diffractogram was taken from CdS powder obtained by removing water from the colloidal solution, in the range of angles 2θ from 15° to 55° in 0.03° steps, at the exposure time 10 s for each

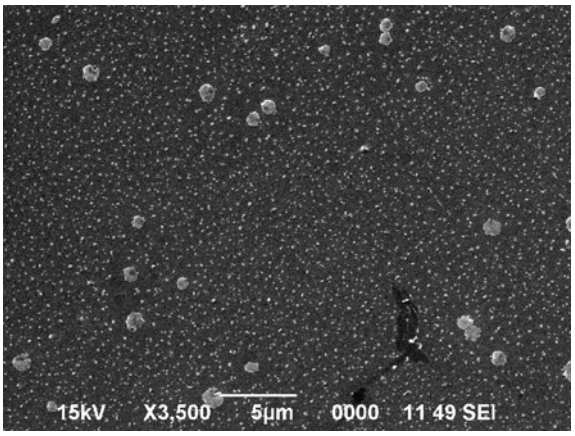
point. The diffraction pattern has three broad diffuse peaks at the angles 27°, 44°, and 52°, which showed that single-crystal particles of CdS forming agglomerates in the colloidal solution have disordered close-packed structure with the space group *P*6*mm* [17]. The disordered close-packed structure of CdS has an identical short-range order like that of large crystalline CdS modifications of the type *B*3 sphalerite and *B*4 wurtzite and differs only in the absence of periodicity in the arrangement of the close-packed layers of cadmium and sulfur. This structure is characteristic of nanostructured powders and films of cadmium sulfide with particle sizes less than 14 nm [18].

By approximation of the diffraction maxima by the pseudo-Voigt function we determined their broadening, which amounted to 5°, 2.6°, and 3° for the peaks at the angles 27°, 44°, and 52° respectively. Such a strong broadening of the intensity maxima indicates the small size of the coherent scattering areas (CSA). The size of the CSA was defined both by direct calculation of the diffraction patterns from the model of a disordered structure of the CdS nanoparticles with the Debye formula [19], and with the Scherrer formula $D = K\lambda/B\cos\theta$, where the form-factor $K = 1$, the wavelength of CuK_α radiation $\lambda = 0.154$ nm, B is the broadening of the peaks in radians, $\theta = 2\theta/2$ is the incidence angle of the beam.

For example, calculation by Scherrer showed that the CdS nanoparticle size ranges were within 2.7± 0.9 nm, whereas the calculation using the Debye formula showed approximately close, but somewhat smaller size of the particles, in the range of 1 to 2 nm.

Optical fluorescence analysis. For studying fluorescent properties of the synthesized colloidal particles and monitoring their growth in solution was used an optical microscope Leica DM 2500 M, equipped with a mercury UV lamp and filter in the wavelength range from 335 to 425 nm. Colloidal particles were placed on silicon supports by briefly vertical dipping the supports in the solution for 15 s.

Optical measurements showed that the fluorescence does not depend on the duration of keeping the CdS particles placed on the support, i.e., after removing the dispersion medium the disperse phase does not change its fluorescent properties over time. At the same time, it was found that the fluorescence changed significantly depending on the duration of keeping the solution. Thus, freshly prepared and kept for one day colloidal solutions had a green fluorescence, the two-day solutions had green and red areas, and the solutions kept longer than two days had only orange fluorescence.



Electron micrograph of particles of the disperse phase of CdS colloidal solution 1 month after the solution preparation. Under the microscope at a magnification of 3500 times are seen the particles of the size 10 nm, 100 nm, and some agglomerates of irregular shape of the size 1 μm.

Electron microscopy analysis. The microstructure of CdS nanoparticles was studied by scanning electron microscopy. Analysis of the microstructure of the samples, the measurement of the size of grains and agglomerates was carried out on a scanning electron microscope JEOL JSM 6390 LA in secondary electrons. The chemical composition of the investigated particles was determined by X-ray energy dispersion analysis, which confirmed the nearly stoichiometric composition of the sulfide phase.

Electron microscopy analysis allowed to confirm visually the observed stability of the obtained colloidal solution. The solution remains clear at room temperature for one month from the date of its preparation and for four months when kept at 4°C. Indeed, the particle size of the dispersed phase in a visually transparent colloidal solution does not exceed 10 nm. In the course of keeping the solution gradually loses its transparency due to the loss of the aggregative stability. The loss of sedimentation stability is seen in the emergence and accumulation over time of a precipitate at the bottom of the reaction vessel. According to the electron microscopic studies, the disperse phase of CdS colloidal solution stored at room temperature for one month after preparation of the solution partially agglomerated, and the size of coagulates and their number increased in time. The figure shows the electron micrograph of CdS particles

1 month after the preparation of solution. Under the microscope at a 3 500 times magnification particles are seen of the size 10 nm, 100 nm, and some agglomerates of irregular shape of the size 1 μm. These values are not of the same order of magnitude as the data of X-ray analysis. Therefore, it can be stated that the large-scale (100 nm or more) particles observed with the use of the scanning electron microscopy are agglomerates formed by nanoparticles of cadmium sulfide. After 4 months from the date of preparation, the solution loses its transparency, and the dispersed phase consists of the coagulates of the size 1 μm.

CONCLUSIONS

By the method of chemical condensation we obtained stable aqueous colloidal solution of CdS nanoparticles. Owing to the presence of four-charged ions of ethylenediaminetetraacetic acid Y^{4-}, adsorbed on the surface of CdS nanoparticles, the nanoparticles becomes negatively charged. The ions Y^{4-} are strongly bound to the CdS surface that determines the long-term aggregation and sedimentation stability of the aqueous colloidal solution of CdS.

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