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Synthesis of CdS Nanocrystalsin the Gelatin Matrix with Different pH Values and their Optical Properties

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We have investigated the influence of solution pH on the formation of nanocrystals and their size in the process of synthesis. We have analyzed the optical absorption spectra and luminescence of colloidal solutions of NC CdS.Nanocrystals of cadmiumsulphide were obtained by sol-gel technology in gelatin solution which has different pH values (6 ÷ 10). A decrease was observed in the average size of the nanocrystals from 8 till 3.5 nm while reducing pH from 10 to 6. There has been established the dependence of the contour of luminescence spectra from pH values.

Keywords: cadmiumsulphide; colloidalsolution; luminescence; nanocrystals; opticalabsorption.

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Introduction

The unique properties of nanoparticles of wide-gap semiconducting compounds of A_2B_6 are making prospective their use in the analytical chemistry, in optoelectronic and photovoltaic devices, optical amplification media for telecommunications, in photocatalysis. Semiconductor nanocrystals have a high level of sensitivity and photostability. This causes considerable interest in many fields of research. Semiconductor nanocrystals (NCs) are used for the development of information technology, physics of solar cells, nanoelectronics, optics, molecular and cellular biology, in medical diagnosis [1, 2]. One feature of isolated nanocrystals in the polymer matrix is a high chemical activity of the surface and the consequent need to consider interfacial electronic and physicochemical processes at the interface of nanocrystal-matrix. They develop and affect on the optical and luminescent properties of quantum dots under the influence of various external factors (temperature, type of stabilizer, the concentration of the initial components and ratios, pH, etc.) [3].

The purpose of this work is to obtain CdS nanocrystals in gelatin matrix for different values of the solution pH and to investigate the influence of this value on the optical absorption and luminescence.

I. Experimental

The object of research were nanocrystals of cadmium sulfide that were obtained by the sol-gel technology [4] from solutions of salts cadmium (cadmium nitrate) and sulfur (sulphide sulfur) in the colloidal solution of gelatin. The formation of CdS particles as a result of exchange reactions: $Cd(NO_3)_2 + Na_2S = CdS + 2\ NaNO_3$. The pH of the solutions was varied by adding of alkaline solution or hydrochloric acid and measured by ionomer. Solutions had color from light yellow (for pH = 6) to dark yellow (for pH = 10). After completion the synthesis process, the solution which contained suspended in the gelatin nanoparticles of CdS, was sprayed on glass substrates and dried to hardening gelatin gel - the process of polymerization of gelatin.

Average radiuses of cadmium sulfide nanocrystals r were evaluated from the optical absorption spectra by using expressions for the threshold energy of interband absorption. According to the theory of interband absorption [5], in the absorption spectrum should be observed series of discrete lines. Absorption threshold (the energy of the first optical transition, called the effective band gap of the nanocrystal) is the magnitude of:

$$hw_{01} = E_g + \frac{\mathbf{h}^2 p^2}{2 m r^2} \qquad (1),$$

where Eg - the optical band gap of bulk crystal; $m = \frac{m_e m_n}{m_e + m_n}$ - the reduced mass of electron and hole; r - average radius of the nanoparticle. From here can be seen the law under which the effective width of the band gap increases with the decrease of the radius of nanoparticle.

The optical absorption spectra were measured on an SF-26 spectrophotometer in the wavelength area from 320 nm to 600 nm. For reduce the errors associated with the influence of light scattering in the short-wave area (320 - 360 nm) there was used filter USF-2 for cutting the visible area of the spectrum. Measurement error did not exceed ± 1 %. Luminescence was excited by pulse laser LCS-DTL-374QT with a wavelength 355 nm excitation of light. The maximum laser power was 35 mW.

II. Results and Discussion

We have received CdS nanocrystals in gelatin solution which has different pH values (6 ÷ 10) and investigated spectra of optical absorption and luminescence of colloidal solutions of CdS nanocrystals, synthesized in the given conditions. Also have been explored these characteristics depending on the time storage of samples in air.

The absorption spectra of CdS nanocrystals with different values of pH: 6 (1) 8 (2) 10 (3) shown in Figure 1. In all cases been a shift of the absorption edge towards higher energy than the band gap of bulk single crystal of cadmium sulfide (E_g = 2,5 eV). When changing the pH value from 10 to 6 average size of synthesized nanocrystals decreases from 8 to 3.5 nm.

The observed behaviors of the absorption spectra NC CdS can be explained as follows. Used in the synthesis of aqueous solutions of the reactants of the reaction. This hydrolysis cadmium salts and sulfur, wherein the distribution of the products of hydrolysis depends on the pH [6]. Thus, at pH < 6 present in the solution in a large amount of cadmium Cd^{2+} ions and small quantity of ions HS^-. The size of nanocrystals in this case, will limit the amount of hydrogen sulphide ions. In the pH range 7 ÷ 8 of cadmium ions and ions of hydrogen sulfide are equalized, thereby increasing the size of the nanocrystals.

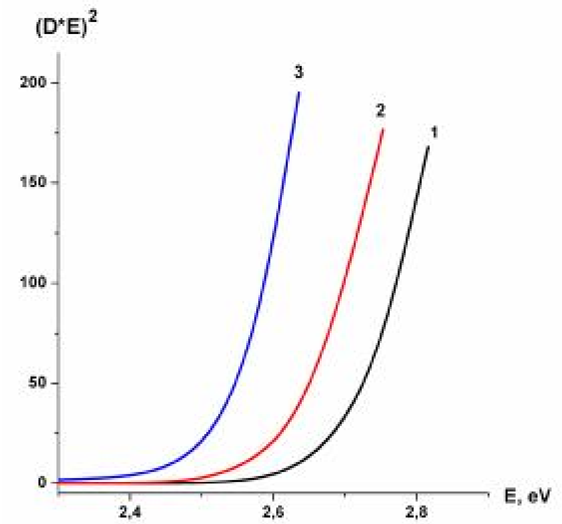

Fig. 1. The optical absorption spectra of nanocrystals CdS, obtained at pH values: 6 (1), 8 (2), 10 (3).

At pH > 8 cadmium ions decreases, but increases the concentration of hydroxide cadmium ions $CdOH^-$and ions HS^-, which leads to further growth of the nanocrystals. This is observed in the absorption spectra (Figure 1).

In this paper we studied the effect of the molar composition of the solution on the emission spectrum of the NC. From the literature it is known that in nanocrystals of cadmium sulfide luminescence in the visible spectrum has a short wavelength band, the nature of which is associated with band-to-band or the exciton recombination [7]. The nature of luminescence wavelength bands associated with the defects, which may be located in the bulk and on the surface. These are the intrinsic defects (vacancies of cadmium and sulfur), and the association of these defects and their possible impurities [8]. Changing the content of sulfur and cadmium ions in solution, the surface of NC may contain in excess of one or another ion.

Figure 2 shows the luminescence spectra of the

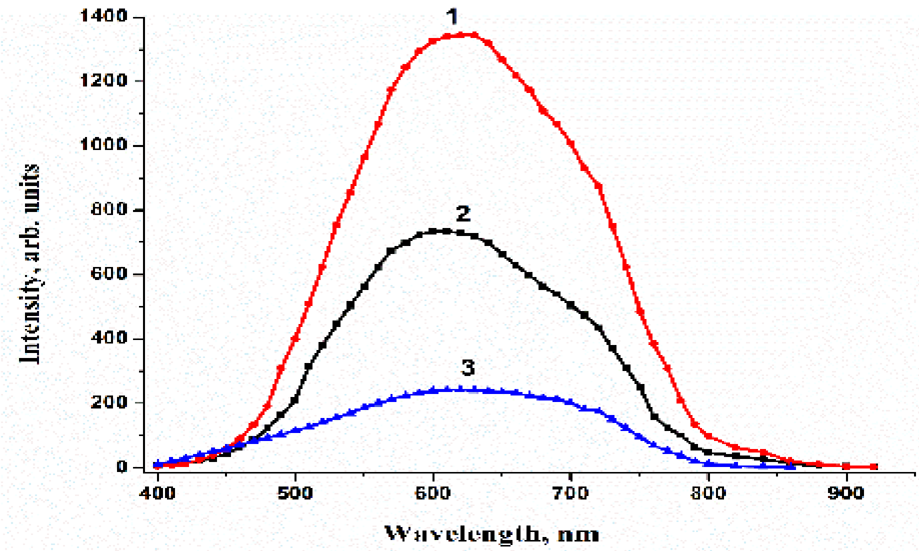

Fig. 2. The luminescence spectra of nanocrystalsCdS, obtained at a pHvalues: 6 (1), 8 (2), 10 (3).

investigated colloidal solutions of nanocrystals obtained at different pH values (6, 8, 10). In all samples in the emission spectrum prevails wide-wavelength luminescence band with a maximum localized around 600 nm. Notably, that this band is a complicated and contour of luminescence spectra varies according to pH values. With the increase of the pH value in the contour of the luminescence band appears a long-wavelength band.This fact indicates a change in the concentration of defects responsible for radiative (emitting) recombination [9]. Furthermore, it is seen that increasing the pH value of 6 (curve 1), 10 (curve 3) integrated intensity of luminescence decreases.

This fact agrees with the results of luminescent nanostructure CdS with shell ZnS, given in [7]. Authors of this paper noted that in whereas the spectrum of luminescence of samples, obtained with low pH values , is characterized by longwave band and does not change, the samples prepared at pH > 8, have a broad spectrum of luminescence, extending into the short range.So change in the acid-alkaline balance causes a formation of nanocrystals of different size and stoichiometry of atoms on their surface. In acidic environments will be formed nanocrystals with an excess of cadmium on the surface, and alkali - with an excess of sulfur [9]. Furthermore, at pH> 8 in the solution is formed the hydrolysis product - cadmium hydroxide. Its concentration will increase with increasing pH.With increasing pH value increases sulfur in the solution and on the surface of NC. While the luminescence intensity decreases. This fact indicates that the sulfur in NC suppresses the luminescence of cadmium sulfide and for the long-wavelength luminescence can be responsible sulfur vacancies [7].

For the identification of the components of the long-wavelength luminescence, we carried out the analysisusingGaussian curves. The position of the maxima of the luminescence bands components are shown in Table 1. At pH = 6 and pH = 8 the luminescence spectra of the colloidal solutions is observed two and in samples with pH = 10 - three luminescence bands. Here appears an additional short-wavelength band with λ = 470 nm, which is localized at the edge of the absorption spectrum.

Table 1

Dependence of the position of calculated maximum of luminescence of NCCdS on the pH values of solution

pH	$\lambda_{1,\ nm}$	$\lambda_{2,\ nm}$	$\lambda_{3,\ nm}$	$I_{\lambda 2}/I_{\lambda 3}$
6	-	593	701	1,7
8	-	590	700	1,83
10	470	608	711	2,74

The edge luminescence in CdS nanocrystals is usually recorded in the samples with modified surface. Moreover, as known from the literature, such surface modification can be carried out under suitable conditions of synthesis due to the shell of cadmium hydroxide [2]. Increased alkalinity of the solution at pH > 8 hydroxide promotes the formation of the shell and there is a possibility of precipitation of the compound on the surface of nanocrystals, which ensures the passivation of surface states.Intensity ratio of components bands $I_{\lambda 2}/I_{\lambda 3}$ (see Table 1) with increase the alkalinity decreases, which supports the hypothesis on the nature of the long component.

Conclusion

By the method of colloidal chemistry with the use of gelatin as a stabilizer were obtained nanocrystals CdS that had bright luminescence in the long wavelength area. There were observed the influence of the solution pH on the nanocrystal size, namely a decrease in average size NC from 8 to 3.5 nm with decreasing pH from 10 to 6. The forming nanocrystals of different size is connected with changes in acid-base balance as a result of hydrolysis of salts components. The luminescence in the long wavelength region of the spectrum is associated with defects on the surface of the nanocrystals CdS, namely with sulfur vacancies.

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