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TECHNOLOGICAL FEATURES FORMATION SPECTRA OF LUMINESCENCE CdS QD

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It are presented the results influence of two parameters of synthesis process of quantum dots sulfide cadmium (CdS QD) on the spectrum luminescence, namely, the acid-base balance of the growth solution and the correlation of reaction components (cadmium and sulfur salts). Carried out the syntheses in which the pH solution was changed in the interval of values from 2 to 10. There were also synthesized CdS QD with different ratios of the initial components. The results obtained by evidence of the fact that the technological process has a significant impact on the formation of bands luminescence CdS QDs . In both cases, the luminescence spectrum had three bands that are localized at λ_1 = 462 ÷ 493 nm, λ_2 = 555 ÷ 598 nm, λ_3 = 660 ÷ 711 nm. The observed features of the effect of these technological factors on the spectrum luminescence of CdS QDs are explained by the fact that, in the synthesis, the concentration of cadmium and sulfur ions is a determining parameter. In the first case, the ion concentration is controlled by the pH value of the solution, and in the second, by the initial concentration of $Cd(NO_3)_2$ and Na_2S.

INTRODUCTION

Semiconductor CdS QDs are cause significant interest due to their unique properties, which are absent in bulk materials due to the effect of quantum limitation of charge carriers. For a number of fields of science and technology, colloidal quantum dots are promising materials. They are of particular interest as a basis for creating biomedical markers and sensors [1].

From the point of view application of quantum dots (QD) of A_2B_6 compounds, their luminescent properties are of the greatest interest. The study of the luminescence of CdS QDs is a fairly large amount of work, however, the question of which luminescence bands are caused by intrinsic and impurity lattice defects and how the technology conditions affect the formation of the luminescence spectrum of CdS QDs remains topical [2]. In modern literary sources, only the possibility of the existence of defects is mentioned, but no attention is paid to the disclosure and description of their nature and the conditions of their creation in the process of synthesis [3]. This issue also includes the development of controlled synthesis of QDs, during which they form their own defects that determine the luminescence spectrum.

The colloid-chemical synthesis of CdS QDs is influenced by a large number of factors related to the conditions of the synthesis (duration, rate of introduction of the reaction components, temperature of synthesis). The formation of luminescence centers in CdS QDs depends on the concentration of cadmium and sulfur ions and their ratio, as well as on the acid-base balance in an aqueous growth solution. The results of the influence of these factors are presented in this study.

1. DESCRIPTION OF OBJECTS AND METHODS OF RESEARCH

The cadmium sulfide nanocrystals under study were obtained by a chemical method from solutions of cadmium and sulfur salts in a colloidal solution of gelatin. The formation of CdS particles occurs as a result of the exchange reaction: $Cd(NO_3)_2+Na_2S \Rightarrow CdS+2NaNO_3$.

The pH value of the solutions was changed by adding a solution of alkali or hydrochloric acid to an aqueous solution of gelatin with cadmium nitrate to obtain the necessary pH values (2 ÷ 10).

The pH value of the solutions was changed by adding a solution of alkali or hydrochloric acid to an aqueous solution of gelatin with cadmium nitrate to obtain the necessary pH values (2 ÷ 10). Samples were also synthesized, in which the concentrations of cadmium and sulfur ions and their ratio changed. The pH value in the synthesis process was constant and was equal to 7. In the course of the study, four combinations of solutions with different ratios of the initial components of cadmium and sulfur were created. The ratio of the molar concentrations of the initial components of $Cd(NO_3)_2$ / Na_2S was: 1/4, 1/2, 1/1, 2/1. In each of these combinations, the following samples were obtained: with a constant volume of CdNO3, namely 5 ml, in each of the four combinations, the volume of injected Na2S changed: 0.25; 0.5; 12; 3, 4 and 5 ml. The luminescence was excited by a LCS-DTL-374QT pulsed laser with a wavelength of 355 nm. Laser power - 35 mW.

2. DESCRIPTION AND ANALYSIS OF RESULTS

2.1. Effect of acid-base balance in aqueous solution with Cd CdS.

It is known that salt solutions are carried out in aqueous solutions. In our case, the hydrolysitrate of cadmium and sulfate. The molar concentration of ions is calculated by the formulas (1 - 2) and is graphically presented in Figure 1.

$$C_0 = [Cd^{2+}] + Cd(OH)^+ + Cd(OH)_2^0, \qquad (1)$$

$$\alpha_1 = \frac{|Cd^{2+}|}{C_{Cd(NO_3)_2}} = \frac{1}{1+\frac{k_1}{[H^+]}+\frac{k_1 k_2}{[H^+]^2}}; \quad \alpha_2 = \frac{k_1\alpha_1}{[H^+]}; \quad \alpha_3 = \frac{k_1 k_2 \alpha_1}{[H^+]^2}, \qquad (2)$$

where α - is the molar concentration of the components; k - is the ionization coefficient (taken up from the table [4]).

It is seen that at pH values < 8 the concentration of cadmium ions in solution dominates, and up to pH = 6 it remains unchanged. At pH > 6, the concentration of cadmium ions decreases and $Cd(OH)^+$ is formed. At pH value > 9, cadmium hydroxide $Cd(OH)_2$ is formed.

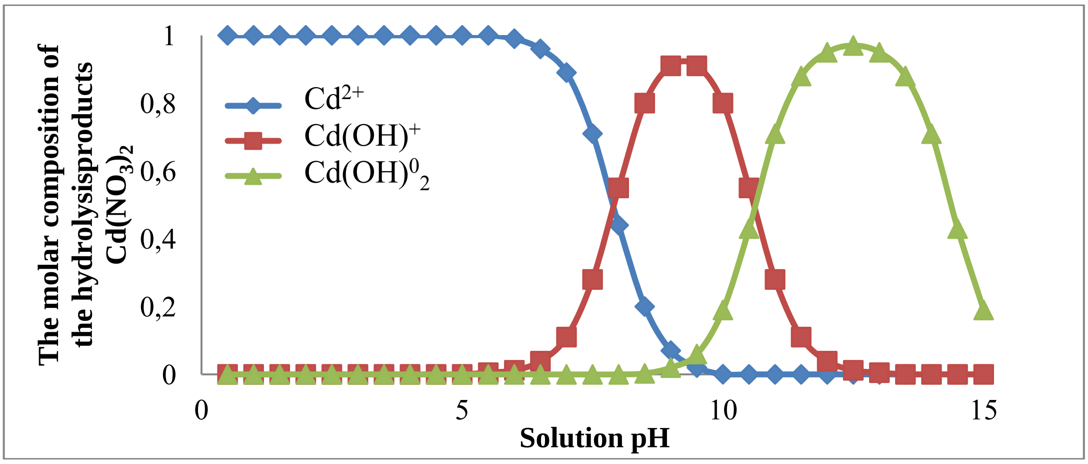

***Fig. 1** - Dependence of ion concentration on solution pH*

Cadmium sulfide nanocrystals were synthesized at the following pH values of the solution: 2, 4, 7, 10. Regarding the hydrolysis of sulfur sulfide, it is known that the hydrolysis of sulfur salts occurs at pH values > 6. At lower pH values, the source of sulfur is impurity sulfur, which is present in gelatin.

In fig. 2 shows the normalized luminescence spectra of CdS QDs, which were synthesized at different pH values. It can be seen that the luminescence spectra of samples obtained at low pH (2 and 4) and at pH (7 and 10) differ sharply. At low pH values, the short-wavelength emission band with a wavelength λ_{max} = (480–490) nm dominates, and at large pH, the longwave band, localized at λ_{max} = (700 - 720) nm.

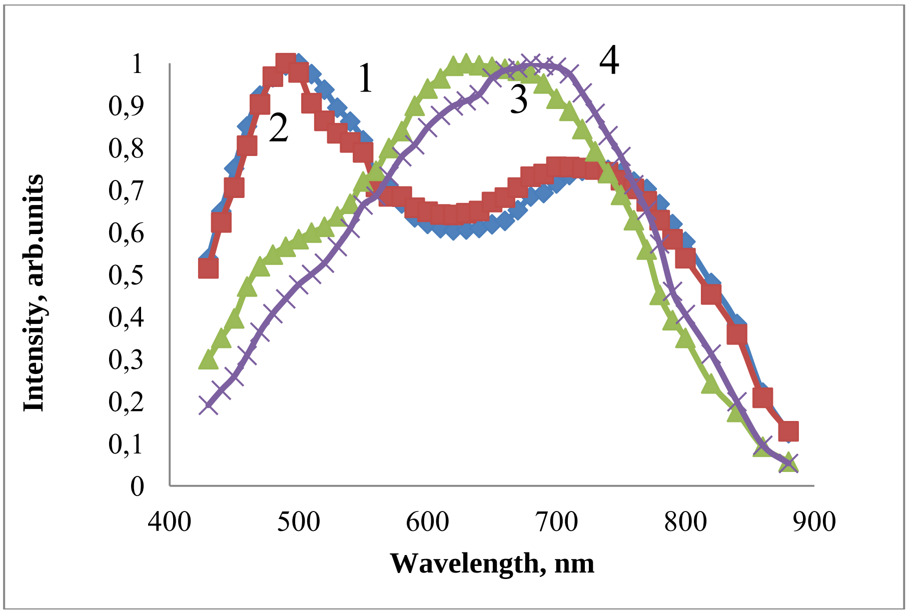

***Fig. 2** – Normalized luminescence spectra of CdS QDs grown at different pH values of the solution: 2 (1), 4 (2), 7 (3), 10 (4)*

2.2. The effect of the relative concentration of the starting components on the fluorescence spectrum of the QD of CdS

The graphs presented in Figure 3 correspond to the relative concentrations of the $Cd(NO_3)_2$ / Na_2S components: 1/4, 1/2, 1/1, 2/1 (Fig. 3 a, b, c, d, respectively). It is seen (Fig. 3 (d)) that with an increase in the concentration of cadmium, the shortwave (λ_{max} = 490 nm) band is dominant, and in Fig. 3 (a), where the concentration of cadmium is rather low, this band is hardly noticeable. This confirms the nature of the evolution of the spectra of rice. 3 (a, b, c, d) in which Na_2S was added to the initial solution: 0.25; 0.5; 12; 3, 4 and 5 ml, (curves 1-7), respectively. Indeed, it can be seen that the addition of sulfur contributes to an increase in the intensity of the long-wavelength band. In experiments, samples containing a short-wavelength emission band (λ = 462 ÷ 493 nm) have an excess of cadmium, and a long-wavelength band (λ = 660 ÷ 711 nm) is an excess of sulfur.

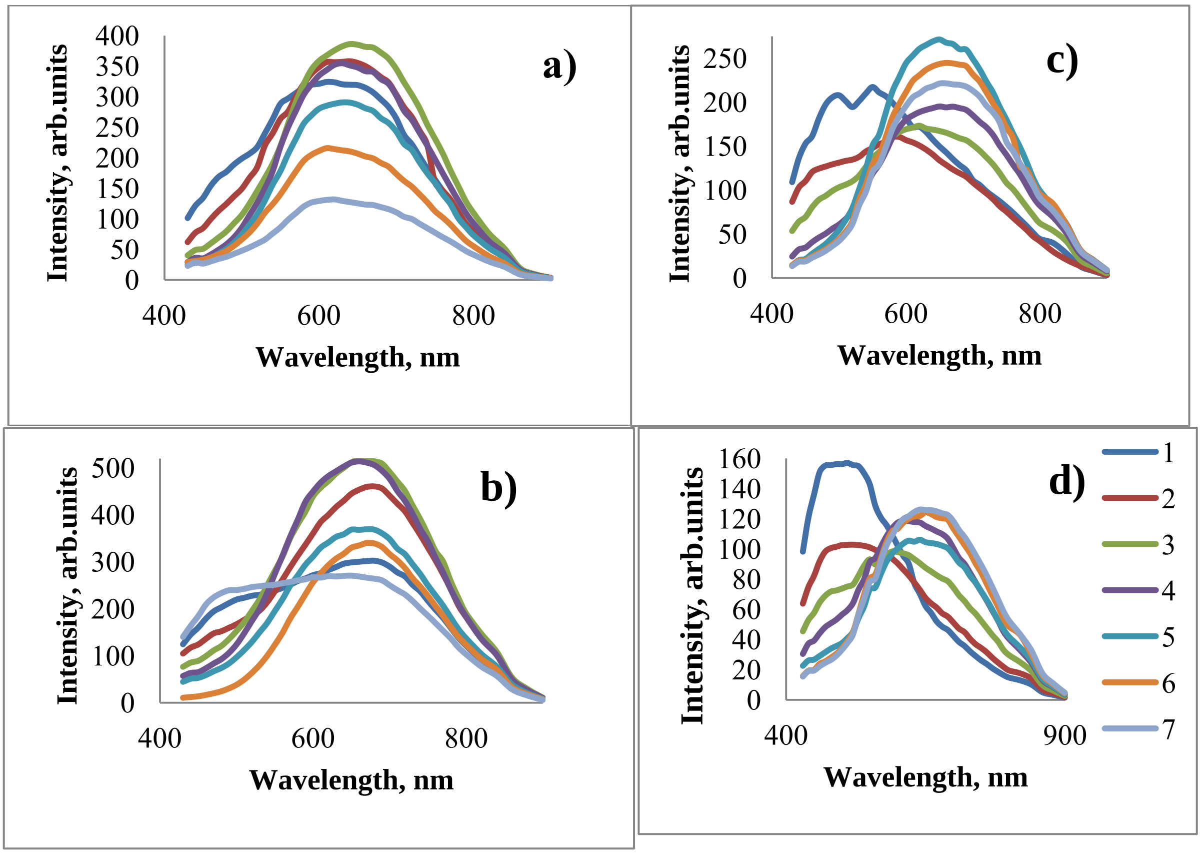

Fig. 3 *– Spectrum of luminescence CdS obtained at a molar ratio of the original components of $CdNO_3$ / Na_2S: 1/4 (a); 1/2 (b); 1/1 (c); 2/1 (d).*

Since the curves of the luminescence spectra in both experiments are complex and consist of several elementary bands, the approximation of the luminescence spectra by Gauss curves was carried out, with the result that three bands of emission in CdS were identified. The results of decomposition are shown in table 1.

Table 1. Dependence of the positions of the maximums of the luminescence bands of QDs, obtained as a result of the decomposition of the spectrum, on the value of the solution and for different ratios of the original components

Effect of acid-base balance in aqueous solution with QDs CdS (Fig. 2)				*The effect of the relative concentration of the starting components on the PL of QDs of CdS (Fig. 3)*			
pH	λ_1, nm	λ_2, nm	λ_3, nm	*$CdNO_3$ /Na_2S*	λ_1, nm	λ_2, nm	λ_3, nm
2	490	-	716	*2/1 (curve 1)*	462	555	660
4	493	-	708	*1/1 (curve 3)*	462	573	690
7	483	592	694	*1/2 (curve 5)*	464	598	703
10	481	578	703	*1/4 (curve 7)*	-	593	711

Note that in the photoluminescence spectra of nanocrystals, the band in the region λ = 555 ÷ 598 nm is also recorded. This band develops in nanocrystals, the synthesis of which was carried out at the same concentration of cadmium and sulfur ions.

Thus, the above results indicate that the luminescence of CdS QDs obtained by the method of colloidal chemistry due to its own defects and this is due to the influence of the stoichiometric composition of cadmium and sulfur. Some discrepancy in the localization of the luminescence maxima of individual bands can be explained by the spread in the size of the QD.

CONCLUSIONS

In this work, the influence of two parameters of the process of QD synthesis on the spectrum of their luminescence, namely, the acid-base balance of the growth solution and the ratio of the components of the reaction (cadmium salts of sulfur), is investigated. Syntheses were carried out in which the pH of the solution varied in the range of values from 2 to 10. Also, CdS QDs were synthesized with different ratios of the starting components.

The results obtained indicate that the technological process has a significant impact on the formation of cadmium sulfide QD emission bands. In both cases, the emission spectrum had three bands, which are localized in the wavelength range $\lambda_1 = 460 \div 490$ nm, $\lambda_2 = 555 \div 598$ nm, $\lambda_3 = 660 \div 720$ nm. The observed features of the influence of these technological factors on the luminescence spectrum of CdS QDs are explained by the fact that, in the synthesis, the determining parameter is the concentration of cadmium and sulfur ions. In the first, the ion concentration is regulated by the pH of the solution, and in the second, by the initial concentration of $Cd(NO_3)_2$ and Na_2S.

RERERENCE

1. The nature of the luminescence centers in CdS / [VG Klyuev, Fam Thi Khan Mien, Yu. S. Bezdetko] nanocrystals. - Condensed matter and interphase boundaries, V. 16, № 1, 2014. - 27 p.
2. Features of the formation of CdS nanocrystals at a fixed synthesis time / [Yu. S. Bezdetko, V. G. Klyuev]. - Bulletin of VSU. Series: Physics. Mathematics, № 1, 2014. - 6 p.
3. Quantum Dots Synthesized Morphological and Optical Properties of CdS with different pH values / [Akeel M. Kadim, Wasan R. Saleh]. - Iraqi Journal of Science, Vol. 58, No.3A, 2017. – 1207 p.
4. Hydrolysions of metals in diluted solutions / [V. A. Nazarenko, V. P. Antonovich, E. M. Nevskaya]. - M. : Atomizdat - 1979. - 192 p.