Journal of Nano- and Electronic Physics
Vol. **11** No 3, 05031(4pp) (2019)

Журнал нано- та електронної фізики
Том **11** № 3, 05031(4сс) (2019)

Influence of Technology on the Formation of Luminescence Centers in CdS Quantum Dots

V.A. Smyntyna[1], V.M. Skobeeva[2], K.A. Verheles[1], N.V. Malushin[2]

[1] *I.I. Mechnikov National University of Odesa, 2, Dvoryanskaya St., 65082 Odesa, Ukraine*
[2] *I.I. Mechnikov National University of Odesa, 27, Paster St., 65082 Odesa, Ukraine*

(Received 17 June 2019; revised manuscript received 24 October 2019; published online 25 October 2019)

The paper describes results of the research on the effect of the synthesis of cadmium sulfide quantum dots by the colloid-chemical method in an aqueous solution of gelatins on their optical and luminescent properties. It was shown that to understand the mechanism of the formation of defects in CdS QDs when they are synthesized in aqueous solutions of salts, it is necessary to take into account the result of the hydrolysis process and the dependence of its products on the pH of the solution. Based on the calculation of the molar concentration of the components of the hydrolysis of the cadmium salt $Cd(NO_3)_2$, the conclusion was drawn about the types of intrinsic defects that determine the observed photoluminescence spectrum of CdS QDs.

Keywords: Cadmium sulfide quantum dots, Intrinsic defects in CdS QDs, Absorption, Photoluminescence.

DOI: 10.21272/jnep.11(5).05031 PACS numbers: 78.30.Jw, 78.67.Hc

1. INTRODUCTION

CdS quantum dots (QDs) have aroused considerable interest due to their unique properties, which are absent in bulk materials due to the effect of quantum retention of charge carriers [1, 2].

Among the main distinguishing QDs properties should be highlighted the size dependence of the photoluminescence (PL) wavelength, a high quantum yield of PL, an extended absorption spectrum, which makes it possible to excite the luminescence of different sizes QDs with a single radiation source, small sizes, which provide a high penetrability of particles. In addition, compared to classical organic fluorophores, QDs are more resistant to photobleaching and, thus, suitable for long-term studies [3]. The possibilities of the diverse application of nanocrystals [4, 5] in optoelectronics led to an intensive search for methods for changing their properties. Successful solution of this problem depends on understanding the processes of formation of the physical properties of QDs during synthesis [6, 7].

From the point of view of application of QDs of A2B6 compounds, their luminescent properties are of the greatest interest.

The study of the luminescence of CdS QDs is devoted to a fairly large number of works, but the question of the nature of the centers that cause luminescence, the conditions for their formation in the synthesis process, still remains relevant. This is due not only to the different ways of obtaining QDs, but also to the fact that wide luminescence bands are usually observed in nanocrystals and this wide band consists of several individual bands.

The colloid-chemical synthesis of CdS QDs is influenced by a large number of factors related to the synthesis conditions (duration, rate of introduction of the reaction components, synthesis temperature, the ratio of the initial components of cadmium and sulfur ions). In addition to the nature and concentration of precursors and stabilizers, the acidity of the *pH* dispersion medium turned out to be an important factor in controlling the optical characteristics of the obtained QDs [8]. The results of studies by different authors on the effect of the acid-base balance of the growth medium on the properties of CdS QDs (QD size, type of intrinsic defects, luminescence spectrum) indicate their ambiguity. Thus, in [9], CdS QDs with a size of 1.1 nm were obtained in alkaline solutions (*pH* 8, 10, 12), while nanoparticles obtained in acidic solutions (pH 4, 5) tended to aggregate with the formation of larger particles (~ 74.5 nm). The authors of [10, 11] did not observe the formation of CdS QDs in an acidic medium (*pH* 2, 4), however, in [12], it was reported that by varying the pH from 1.6 to 2.2, CdS particles with dimensions 3.5-5.3 nm were obtained.

There is also a strong dependence of the size of nanoparticles on the *pH* of the solution in alkaline media. The smallest particles were formed in a weak alkaline medium with a *pH* of 8 due to the lowest concentration of S_2-ions. In a strongly alkaline medium with a *pH* of 12, the particle size is again lower than that of *pH* 10. This is explained by a decrease in the concentration of Cd_2^+ ions due to the increased formation of $Cd(OH)_2$ at higher *pH* values. In this way, *pH* 10 is more favorable for the formation of CdS QDs, for the method described in article [11]. In this work, the conditions for the appearance of exciton luminescence were determined, which the authors attribute to the small size and smaller dispersion.

The study of self-activated luminescence of CdS QDs obtained at different concentrations of the initial components is the work [13]. To explain the nature of the luminescence centers in CdS QDs, the authors used an analogy with the nature of defects in a CdS single crystal. It was shown that, according to the proposed physical model of luminescence centers, the maxima of the self-activated bands in nanocrystals depend on the size of nanoparticles, for example: for 3.2 nm $\lambda_{max} = 490$ nm and for 3.7 nm $\lambda_{max} = 550$ nm. Note that such a significant size dependence of self-activated luminescence, which is due to recombination at deep centers, is not confirmed in other similar studies.

According to the literature, luminescence spectra are observed in CdS QDs, which are broad bands in the spectral range from 450 nm to 800 nm [14, 15]. In the study of photoluminescence spectroscopy of CdS nanoparticles, a wide band was observed at 570 nm, which is explained by recombination of electrons and holes associated with surface defects, and a smaller peak at 678 nm is caused by internal defects, such as sulfur vacancies [9]. Individual luminescence bands of CdS QDs can be observed under certain conditions, for example, when doping [16] or irradiated [17].

An analysis of the review of literature data shows that the formation of luminescence centers in CdS QDs depends on many technological factors, among which the concentration of cadmium and sulfur ions and their ratio is decisive. In this connection, in the aqueous synthesis of CdS QDs, the acid-base balance in the growth solution must be taken into account. The effects of this factor are presented in this study.

2. EXPERIMENTAL

The pH values of the solutions were changed by adding a solution of alkali or hydrochloric acid to an aqueous solution of gelatin with cadmium nitrate to obtain the required *pH* (2-10).

Optical absorption spectra were measured on a SF-26 spectrophotometer in the wavelength range from 320 to 600 nm. To reduce the error associated with the effect of light scattering in the shortwave region (320-360 nm), a USF-2 light filter was used, which cut off the visible region of the spectrum. The measurement error did not exceed ±1 %. The luminescence was excited by a LCS-DTL-374QT pulsed laser with a wavelength of 355 nm. Laser power was 35 mW.

3. RESULTS AND DISCUSSION

It is known, that salt is hydrolyzed in aqueous solutions. In our case – the hydrolysis of nitrate and sodium sulfate. We calculated the concentration of Cd ions according to the formulas (3.1)-(3.4) and the corresponding graphs in Fig. 1.

$$C_0 = \left[Cd^{2+}\right] + Cd\left(OH\right)^+ + Cd\left(OH\right)_2^0, \qquad (3.1)$$

$$\alpha_1 = \frac{\left|Cd^{2+}\right|}{C_{Cd(NO_3)_2}} = \frac{1}{1 + \dfrac{k_1}{\left[H^+\right]} + \dfrac{k_1 k_2}{\left[H^+\right]^2}}, \qquad (3.2)$$

$$\alpha_2 = \frac{k_1 \alpha_1}{\left[H^+\right]}, \qquad (3.3)$$

$$\alpha_3 = \frac{k_1 k_2 \alpha_1}{\left[H^+\right]^2}, \qquad (3.4)$$

where, α is the molar concentration of the components, k is the ionization coefficient (taken from table [18]).

It can be seen that at values up to $pH < 8$, the concentration of cadmium ions in the solution is dominant, and up to pH = 6 it remains constant. At $pH > 6$, the concentration of cadmium ions decreases.

At pH values greater than 9, cadmium hydroxide $Cd(OH)_2$ is formed, and at high pH values, the formation of a shell of Cd hydroxides on a cadmium sulfide nanocrystal is possible.

Cadmium sulfide nanocrystals were synthesized at different pH values of the solution: 2, 4, 7, and 10. The normalized absorption spectra of these CdS QDs are shown in Fig. 2.

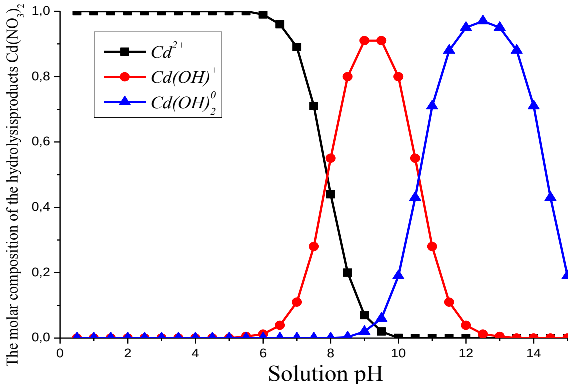

Fig. 1 – Dependence of ion concentration on solution *pH*

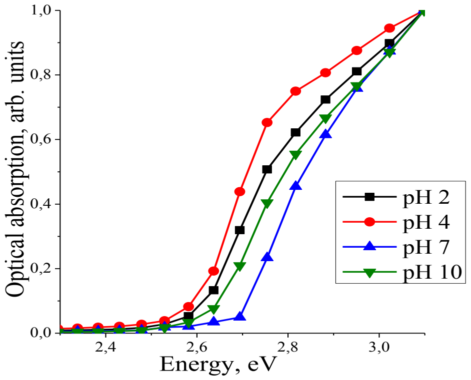

Fig. 2 – The absorption spectra of CdS QDs grown at different values of the solution *pH*: 2, 4, 7, 10

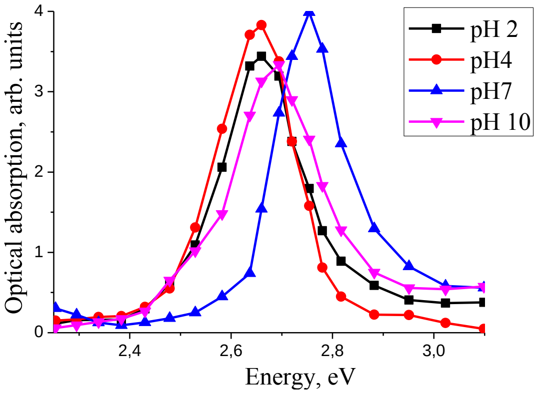

Fig. 3 – Differentiated absorption spectra of CdS QDs grown at various values of solution *pH*: 2, 4, 7, 10

Due to the fact that as a result of the spread in size, in the absorption spectra, there are no maxima corresponding to the optical transitions between the discrete levels, then the reduced experimental curves were differentiated (Fig. 3).

From the analysis of the latter, the values of the energies of the first optical transition, the half-width of the maxima of the differential curves and the size of the QDs were determined. The average radius of QDs was determined using the energy data of the first optical transition. The values of the effective widths of the nanocrystal forbidden zones were also obtained by extrapolating the absorption curves (Fig. 2) to the energy axis, namely, at *pH* 2 and 4 – 2.59 eV, at *pH* 7 and 10, respectively, 2.68 eV and 2.61 eV.

In accordance with Fig. 1 with a lower *pH* (2 and 4), the concentration of cadmium increases, which contributes to the growth of crystals, but with increasing pH (up to 7) the concentration of cadmium ions decreases, as a result – the conditions for crystal growth are limited.

As can be seen from Fig. 1, at lower *pH* values (2 and 4), the concentration of cadmium increases, which contributes to the growth of crystals. With an increase in $pH > 7$, the concentration of cadmium ions decreases, which leads to a limitation of the growth of crystals.

It is known that as a result of the hydrolysis of sulfur salts, S^{2+} ions are formed and this process occurs at high *pH* values (> 9). When $pH > 9$, the formation of crystals and their growth occur with increasing number of sulfur ions.

Fig. 4 shows the normalized luminescence spectra of CdS QDs grown at different *pH* values. The spectra of nanocrystals obtained at low *pH* (2 and 4) differ sharply from those obtained at *pH* 7 and 10. In the spectra of nanocrystals with both low and high *pH* values, a short wavelength emission band with an energy of 2.53 eV is detected. At low *pH*, this band dominates, and at high *pH*, it appears as an inflection on the short-wave edge of the luminescence band curve.

The nature of this luminescence can be attributed to exciton or edge luminescence. At high *pH*, the long-wavelength band localized at a wavelength of $\lambda = 700$ nm dominates, the nature of which is associated with intrinsic defects in nanocrystals.

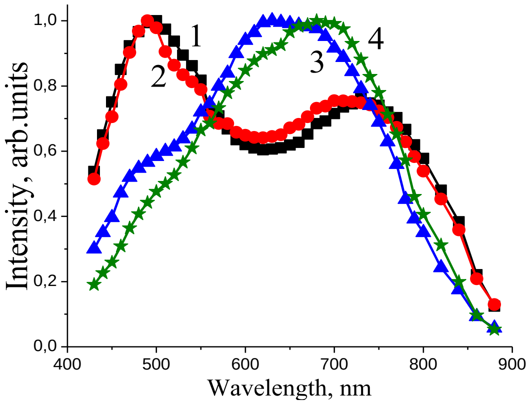

Fig. 4 – Normalized luminescence spectra of CdS QDs grown at different values of the solution *pH*: 2 (1), 4 (2), 7 (3), 10 (4)

Fig. 5 shows the decomposition of the spectra into Gaussian curves. It can be assumed that samples containing a short-wavelength emission band ($\lambda = 470$-498 nm) have an excess of cadmium and thus its nature can be associated with interstitial cadmium and the nature of the long-wavelength band ($\lambda = 716$-754 nm) should be associated with cadmium vacancies.

In the photoluminescence spectra of nanocrystals obtained at values $pH \geq 7$ (Fig. 5c, d), the luminescence in the region of $\lambda = 630$ nm is recorded. According to the results presented in Fig. 1, this band may be due to an associative defect associated with cadmium and sulfur vacancies.

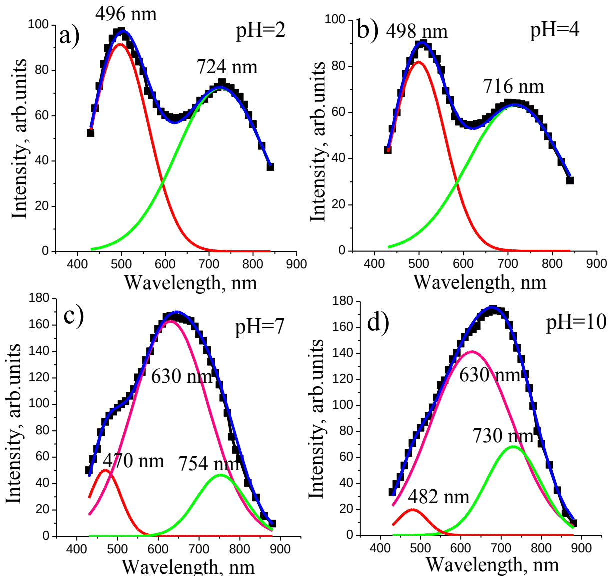

Fig. 5 – Approximation by the Gauss curves of the luminescence spectra of CdS nanocrystals obtained at the values of solution *pH*: 2 (a), 4 (b), 7 (c), 10 (d)

4. CONCLUSIONS

In this work, it was shown that to understand the mechanism of the formation of defects in CdS nanocrystals when they are synthesized in aqueous solutions of salts, one should take into account the result of the hydrolysis process and the dependence of its products on the solution *pH*.

As a result of the calculation of the molar concentration of the components of the hydrolysis of the cadmium salt $Cd(NO_3)_2$, it was found that the values of $pH \leq 8$ concentration of cadmium ions in the solution are dominant. In this case, the shortwave emission band ($\lambda = 470$-498 nm) is due to cadmium interstitials. It is characteristic that the source of sulfur may be gelatin, in which sulfur is an impurity. This fact explains the formation of cadmium sulfide QDs in our technology at low pH values. With the growth of QDs in an alkaline medium, when there is an excess of sulfur ions, the defects that cause the long-wavelength band ($\lambda = 716$-754 nm) are cadmium vacancies. The luminescence in the region of $\lambda = 630$ nm may be due to an associative defect associated with cadmium and sulfur vacancies.

REFERENCES

1. L. Lu, L. Ya-P, M. Ping, C. Wu, J. Feng-L., L. Yi, *J. Membrane Biol* **249**, 757 (2016).
2. W. Aiwu, F. Li, R. Tingke, C. Wen, Y. Muk-Fung, Z. Jiasong, *Optical Materials* **42**, 548 (2015).
3. O.A. Alexandrova, A.O. Drobintsev, I.M. Kvetnoy, Yu.S. Krylova, D.S. Mazing, L.B. Matyushkin, V.A. Moshnikov, S.F. Musikhin, V.O. Polyakova, O.A. Ryzhov, *Nanotechnolog. Nanomater.* **42** No 6, 35 (2015).
4. T. Lavanya, N. Victor Jaya, *Transact. Indian Ceramic Soc.* **70** No 3, 119 (2011).
5. N. Tessler, V. Medvedev, M. Kazes, S. Kan, U. Banin, *Science* **295**, 1506 (2002).
6. Xiong Shenglin, Xi Baojuan, Qian Yitai, *J. Phys Chem.* **114** No 33, 14029 (2010).
7. B. Srinivasa Rao, B. Rajesh Kumar, V. Rajagopal Reddy, T. Subba Rao, *Chalcogenide Lett.* **8** No 3, 177 (2011).
8. Lubomir Spanhel, Markus Haase, Horst Weller, Arnim Henglein, *J. Am. Chem. Soc.* **109** No 19, 5649 (1987).
9. An-QiZhang, Qing-ZheTan, Hui-JunLi, LiSui, Dong-Jin Qian, MengChen, *J. Nanopart. Res.* **16**, 2197 (2014).
10. Akeel M. Kadim, Wasan R. Saleh, *Iraqi J. Sci.* **58** No 3A, 1207 (2017).
11. Jayasheela Uchil, Manjunatha Pattabi, *J. New Mater. Electrochem. Syst.* **8**, 155 (2005).
12. J. Barman, J.P. Borah, K.C. Sarma, *Chalcogenide Lett.* **5** No 11, 265 (2008).
13. V.G. Klyuev, Fam Thi Khan Myen, Yu.S. Bezdetkoi, *Condensed Medium and Interface Borders* **16** No 1, 27 (2014).
14. Pham Thi Hai Mien, V. G. Klyuev, Nguyen Thi Kim Chung, *Condensed Media and Interphase Boundaries* **13** No 4, 515 (2011).
15. D.A. Pomogailo, M.G. Spirin, V.M. Skobeeva, G.I. Dzhardimalieva, S.I. Pomogailo, V.A. Smyntyna, Yu.I. Deniskin, K. A. Kydralieva, *Composites: Mechanics, Computations, Applications: Int. J.* **8** No 2, 171 (2017).
16. V.A. Smyntyna, V.M. Skobeyeva, N.V. Malushin, D.A. Struz, *Sens. Electron. Microsyst. Technol.* **3(9)** No 2, 34 (2012).
17. V. Smyntyna, B. Semenenko, V. Skobeeva and N. Malushin, *Beilstein J. Nanotechnol.* **5**, 355 (2014).
18. V.A. Nazarenko, V.P. Antonovich, E.M. Neva, *Hydrolysis of metal ions in dilute solutions*, 192 (M: Atomizdat: 1979).

Вплив умов технології на формування центрів світіння у квантових точках CdS

В.А. Сминтина[1], В.М. Скобєєва[2], К.О. Вергелес[1], М.В. Малушин[2]

[1] *Одеський національний університет ім. І.І. Мечникова, вул. Дворянська, 42, Одеса 65082, Україна*
[2] *НДІ фізики Одеського національного університету ім. І.І. Мечникова, вул. Пастера, 27, 65082 Одеса, Україна*

У роботі представлені результати дослідження впливу процесу синтезу квантових точок сульфіду кадмію колоїдно-хімічним методом у водному розчині желатини на їх оптичні і люмінесцентні властивості. Показано, що для розуміння механізму утворення дефектів в КТ CdS при їх синтезі у водних розчинах необхідно враховувати результат протікання процесу гідролізу і залежність його продуктів від величини *pH* розчину. На підставі розрахунку молярної концентрації компонентів гідролізу солі кадмію $Cd(NO_3)_2$, зроблений висновок про типи власних дефектів, які обумовлюють спектр фотолюмінесценції КТ CdS, що спостерігається.

Ключові слова: Квантові точки сульфіду кадмію (КТ CdS), Власні дефекти в КТ CdS, Поглинання, Фотолюмінісценція.