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EVOLUTION OF LUMINESCENT PROPERTIES DURING STORAGE CdS QDs IN AIR

This paper presents the results of a study the CdS QDs and nanostructures of CdS / ZnS QDs obtained by the sol - gel technology in an aqueous solution of gelatin and the effect of storage on their luminescence. An increase in the luminescence intensity was found after storage the samples in air. It is revealed that the highest growth factor of the luminescence intensity is observed in CdS QDs without a shell. A mechanism has been formulated that affects the luminescent properties of CdS QDs and nanostructures of CdS / ZnS QDs during storage.

Introduction

One of the most unique properties semiconductor nanomaterials in terms of their practical application is luminescence. In this case, nanocrystals (NC) or quantum dots (QDs) must have an effective emissivity, controlled by the emission spectrum, and stable physical and optical characteristics. Studies of physicochemical and optical phenomena in QDs are relevant for their practical application. [1 – 5].

First of all, interest is the question of how these phenomena depend on the conditions for the synthesis of NCs. In the colloid – chemical method, the physicochemical properties of the obtained NCs are influenced by many factors, including such as: the ratio of the concentrations of the initial components of the chemical reaction, the temperature and speed of the process, the type and concentration of stabilizers limiting the growth of nanocrystals, alloying and introduction of inorganic and organic substances forming shells covering the surface of nanocrystals [6 – 8]. From the point of view of the practical application nanocrystals and nanostructures based on them, the question of the stability the optical, electrophysical, and chemical properties of quantum dots during their storage in air is the interest. Semiconductor NCs are gaining increasing attention for using in light-emitting devices and biological markers. For these applications, important factors are high luminescence efficiency, which is very sensitive to the nature of the particle surface. However, the effect of the surface on radiation hasn't been completely studied. The issue of improving the efficiency of the emitting properties of nanocrystals by technological methods is gaining relevance.

Materials and methods

Cadmium nitrate $Cd(NO_3)_2$ and sodium sulfide Na_2S, as well as zinc salt ZnCl2, which was used to create a CdS NC shell (manufactured by the company "Simestavaal", Odessa), were used as precursors in the synthesis of NC CdS. An aqueous solution of gelatin was used to stabilize the size of the NC.

To measure the optical density spectra, an SF-26 spectrophotometer with a spectral range from 186 to 1100 nm was used. The luminescence spectra were measured using an LCS-DTL- 374QT solid – state laser with pumping, semiconductor diodes operating in the optoacoustic modulation mode.

Synthesis of CdS QDs without and with a shell

In this work, the objects of study were CdS QDs without a shell and CdS QDs covered with a ZnS shell. The synthesis of NCs CdS was carried out by the colloidal - chemical method as a result of the exchange reaction be-

tween the cadmium salt Cd $(NO_3)_2$ and the sulfur salt and Na_2S. 5 ml. is added to an aqueous solution of 1% gelatin an aqueous solution of $Cd(NO_3)_2$ (0.25 mol / L), followed by stirring for 10 min, after which 5 ml. was added dropwise. an aqueous solution of Na_2S (0.25 mol / L).The synthesis reaction took place for 20 minutes at a temperature of 40° C with continuous stirring. As the reaction proceeded, the color of the solution changed from clear to orange.

Our previous studies [7] showed that the build-up of the zinc sulfide shell occurs when an aqueous solution of $ZnCl_2$ and Na_2S is added to the solution in which NCs CdS are synthesized. In this work, the growth of the shell on the CdS NC was carried out at such concentration parameters. In a colloidal solution of 1% gelatin containing CdS nanoparticles, 5 ml. of an aqueous solution of $ZnCl_2$ (0.25 mol/L) was added with the addition of an aqueous solution of sodium sulfide (0.25 mol / L) to the growth reactor. In order to increase the shell thickness, the volume of the added sodium sulfide solution was varied from 1 to 5 ml. With continuous stirring of the solution for 10 minutes, the color of the solution changed from orange to light yellow. The synthesis reaction is as follows (1):

$$CdS + ZnCl_2 + Na_2S \rightarrow CdS/ZnS + 2NaCl \quad (1)$$

The average radius of nanoparticles was estimated by formula (2), in accordance with the theoretical concepts of the theory of absorption in spherical nanoobjects [9].

$$R = \frac{h}{\sqrt{8\mu\Delta Eg}} \quad (2)$$

Here h – Planck's constant; $\mu = ((m_{e^*})^{-1} + (m_{h^*})^{-1})^{-1}$, where $m_{e^*} = 0.19m_e$, $m_{h^*} = 0.8m_e$ are the effective masses of an electron and a hole in cadmium sulfide, respectively, me is the mass of a free electron; ΔE_g is the difference between the band gap in a nanoparticle and a bulk CdS crystal (2.4 eV). The average radius of CdS QDs, according to calculated estimates, was 2.2 nm.

Results and discussion

To study the effect of storage of quantum dots in air on luminescence, the following samples were selected, namely, CdS QDs without a shell, CdS QDs with a shell: CdS / ZnS + Na_2S (1 mL.); CdS / ZnS + Na_2S (2 mL.); CdS / ZnS + Na_2S (4 mL.). It was found that storage of CdS QD samples in uncoated air led to an increase in the luminescence intensity (Fig. 1).

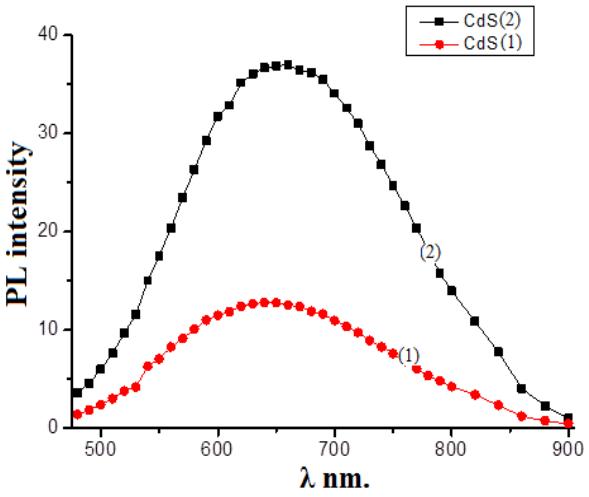

Fig. 1. CdS QD photoluminescence spectra: freshly grown (1), after 5 months of storage (2).

A similar fact of the effect of storage on the luminescence intensity was found in samples of CdS/ZnS QDs prepared with different concentrations of added Na_2S (Figs. 2–4).

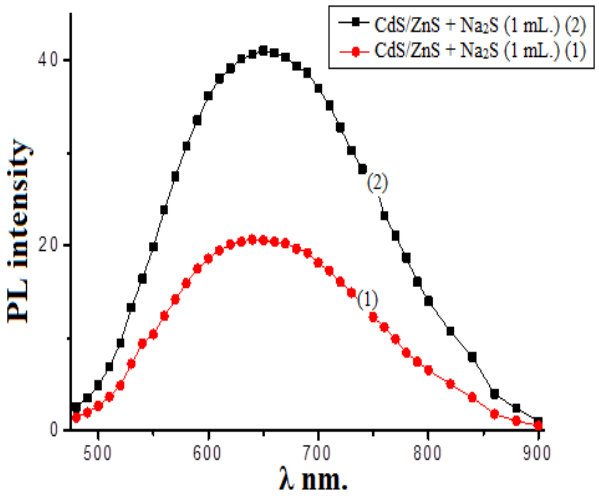

Fig. 2. Photoluminescence spectra of CdS / ZnS + Na_2S (1 mL): freshly grown (1), after 5 months of storage (2).

The data on the change in the intensity of the luminescence bands of CdS QDs, CdS / ZnS nanostructures and the luminescence enhancement factor during storage in air are summarized in Table 1.

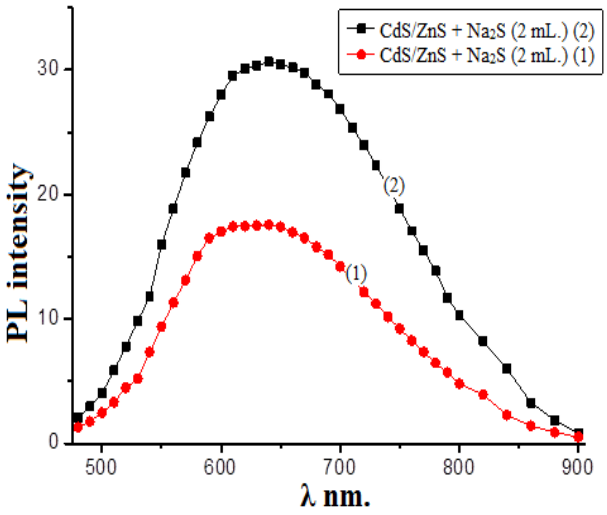

Fig. 3. Photoluminescence spectra of CdS / ZnS + Na_2S (2 mL): freshly grown (1), after 5 months of storage (2).

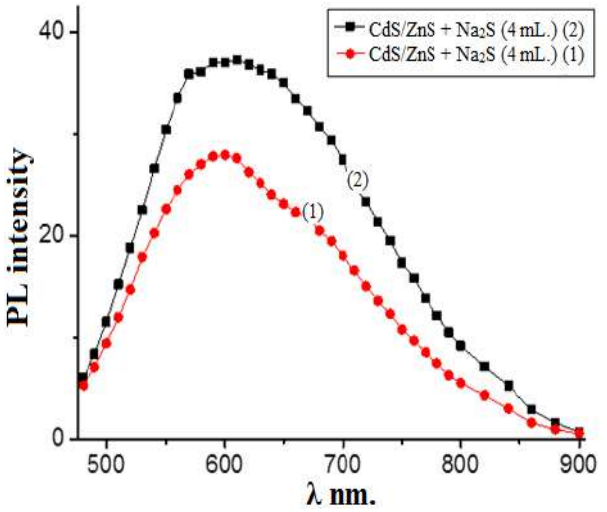

Fig. 4. Photoluminescence spectra of CdS / ZnS + Na_2S (4 mL): freshly grown (1), after 5 months of storage (2).

It is noteworthy that the highest luminescence enhancement factor is observed for the CdS QD sample without a shell and decreases with increasing shell thickness.

Table 1. Data on changes in the intensity of the luminescence bands of CdS and CdS / ZnS QDs during storage in air

Freshly grown samples			After air storage		Gain factor
Sample types	λ, nm.	I, a.u.	λ, nm.	I, a.u.	
CdS	640	12.7	654	37	2.9
CdS / ZnS + Na_2S (1 mL.)	645	21	650	41	1.95
CdS / ZnS + Na_2S (2 mL.)	625	18	640	31	1.7
CdS / ZnS + Na_2S (4 mL.)	596	27	589	37	1.3

To explain the changes in the luminescent properties of the samples under study during long-term storage in air, the mechanisms associated with the features of their structure are considered. Nanocrystals dispersed in matrices are structures containing organic (polymer molecules, organic media, DNA) or inorganic environment (shells of semiconductor compounds). In the case of the complexity of the formation of nanostructures synthesized in colloidal solutions, it is necessary to take into account the influence of the specific conditions of their synthesis, the influence of external factors on the state of the surface of nanocrystals.

For example, in [10], the results of observing an increase in the luminescence intensity of NCs CdSe as a result of their irradiation with UV light are described. The authors explain this phenomenon by the action of the oxidative mechanism: water, penetrating through the gelatinous shell, which is surrounded by CdS NCs, leads to the replacement of gelatin chains attached by amino groups to the surface cadmium atoms by hydroxyl groups. The NCs themselves practically lose the surface layer of cadmium atoms, which are now associated with hydroxyl groups. As a result, conditions are created for the formation of a cadmium hydroxide compound, which can play a coating role for cadmium sulfide nanocrystals. At the same time, a decrease in the size of nanocrystals was observed, which manifests itself in a shift of the absorption spectrum to shorter wavelengths.

The effect of oxygen on the luminescence of CdSe nanocrystals was discovered in the work. [11]. The authors observed an increase in the luminescence intensity of nanocrystals after exposing the samples to air without changing the position of the emission band maximum and the band half-width. The photoelectric effect was not taken into account, since all solutions were in darkness, except for photoluminescence measurements. The authors explain the fact that luminescence is enhanced by the reaction of nanocrystals with dissolved oxygen, which leads to surface passivation. As described in [12], oxygen reacts with NCs CdSe with the possible formation of surface CdO and SeO_2. In addition, CdSe NCs in a growth solution with substances (TOP /

TOPO) did not show an increase in photoluminescence, which confirms the interaction of oxygen with the "bare" surface of nanocrystals.

In our experiment, CdS QDs were synthesized in air without fulfilling the conditions for degassing the growth solution. In this process, similar to [11, 12], the solution will be saturated with oxygen. The NCs CdS were synthesized in a gelatin solution in the open air, which facilitates the saturation of the solution with oxygen. Cadmium ions on the surface of nanocrystals form complexes in the metal associate of several gelatinous molecules surrounding the nanocrystal. Oxygen in a gelatinous medium can interact with cadmium to form cadmium oxide.

Thus, the mechanism for increasing luminescence is the diffusion of oxygen to the surface of cadmium sulfide nanocrystals and the formation of cadmium oxide - CdO. The resulting cadmium oxide will act as the outer coating layer. The luminescence of cadmium sulfide nanocrystals, as a result of this alleged process, will be enhanced. Although thermodynamic reasoning suggests that adsorbed oxygen molecules react with CdS to form surface oxides, the adsorbed oxygen molecules in our samples do not create a macroscopic oxide layer, which can lead to a decrease in the NC size, as well as a loss of photoluminescence efficiency.

Our results show that when the proposed mechanism is implemented, the luminescence enhancement factor for CdS / ZnS samples relative to CdS QDs without a shell should decrease, which is observed in our experiment (see Table 1).

Thus, the results obtained on the evolution of the properties of colloidal CdS nanocrystals indicate the complexity of physicochemical processes occurring during synthesis in open air and the need to take into account the interaction between the nanocrystal surface and the environment, namely, with oxygen.

Conclusion

This work describes the results of studies of changes in the optical properties of CdS nanocrystals and nanostructures of the core-shell CdS / ZnS type during storage in air. Experimental data are demonstrated that indicate an increase in the QD luminescence intensity during storage in air. It was revealed that the highest growth rate of photoluminescence during storage is observed for CdS nanocrystals without a shell. A mechanism is proposed for improving the luminescence intensity associated with the adsorption of oxygen and the passivation of the surface of CdSnanocrystals through the formation of cadmium oxide on their surface.

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Summary This paper presents the results of a study of the of CdS QDs and nanostructures of CdS / ZnS QDs obtained by the sol - gel technology in an aqueous solution of gelatin and the effect of storage on their luminescence. An increase in the luminescence intensity was found after storage of the samples in air. It is revealed that the highest growth factor of the luminescence intensity is observed in CdS QDs without a shell. A mechanism has been formulated that affects the luminescent properties of CdS QDs and nanostructures of CdS / ZnS QDs during storage.

Key words: Luminescence, cadmium sulfide, zinc sulfide, core-shell nanostructure, storage in air.

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ЕВОЛЮЦІЯ ЛЮМІНЕСЦЕНТНИХ ВЛАСТИВОСТЕЙ ПРИ ЗБЕРІГАННІ КТ CdS У ПОВІТРІ.

Резюме В роботі представлені результати дослідження КТ CdS та наностуктур КТ CdS / ZnS, отриманих методом золь - гель технології в водному розчині желатини і впливу зберігання на їх люмінесценцію. Виявлено зростання інтенсивності світіння після зберігання зразків на повітрі. Виявлено, що найбільший коефіцієнт зростання інтенсивності люмінесценції спостерігається в КТ CdS без оболонки. Сформульовано механізм, що впливає на люмінесцентні властивості КТ CdS та наностуктур КТ CdS / ZnS при їх зберіганні.

Ключові слова: Люмінесценція, сульфід кадмію, сульфід цинку, наноструктура ядро-оболонка, зберігання на повітрі.

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ЭВОЛЮЦИЯ ЛЮМИНЕСЦЕНТНЫХ СВОЙСТВ ПРИ ХРАНЕНИИ КТ CdS НА ВОЗДУХЕ.

Резюме В работе представлены результаты исследования КТ CdS и наностуктур КТ CdS / ZnS, полученных методом золь - гель технологии в водном растворе желатины и влияния хранения на их люминесценцию. Обнаружен рост интенсивности свечения после хранения образцов на воздухе. Выявлено, что наибольший коэффициент роста интенсивности люминесценции наблюдается в КТ CdS без оболочки.Сформулировано механизм, влияющий на люминесцентные свойства КТ CdS и наностуктур КТ CdS / ZnS при их хранении.

Ключевые слова: Люминесценция, сульфид кадмия, сульфид цинка, наноструктура ядро - оболочка, хранение на воздухе.

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