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Influence of Organic Molecules on the Luminescent Properties of Composites Based on CdS Quantum Dots

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The influence of methylene blue (MB) and acridine yellow (AY) dyes on the spectra of luminescence of CdS with quantum dots (QD) dye composites is investigated. It is shown that the luminescence spectrum of the heterosystem of nanocrystals (NC) CdS – the dye depends on the absorption region of it. The spectrum of the luminescence of the quantum dots is shifted to the red region by the introducing into colloidal solution of the MB dye and in a case of the insertion of AY the spectrum is shifted into the blue region. The obtained results are explained in a point of view of the transferring the energy from the CdS quantum dots to the dyes by the Forster mechanism.

Key words: quantum dot, dye, luminescence, mechanism of energy transfer.

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Introduction

One of the features of crystals having a nanoscale range and isolated in a polymer matrix is the essential chemical activity of its surface. Therefore, experimental studies of nanosystems with nanocrystal matrix between the phase boundaries and the study of processes occurring on this boundary are relevant. Heterogeneous systems contain nanocomposites and nanostructures created by nanoobjects with different optical characteristics. Properties of such nanostructures are due to the presence of heterogeneities, boundaries, which lead to complex interactions of the electromagnetic field with structural elements.

Particular importance is the study of complex hybrid systems, consisting of semiconductor quantum dots (QD) and biologically active molecules. Colloidal quantum dots (CdS, CdSe, CdTe, ZnS, ZnSe) with porphyrin molecules, phthalocyanines, dyes could be useful as models of hybrid nanostructures for various applications. The urgency of the research of such nanosystems is due, firstly, to the possibility of generating generalizations of physical interactions between the components of heterocomposites, and secondly, a large range of applications in photocatalysts, photovoltaic devices, biosensors that are promising for introduction into biomedicine and environment [1- 6].

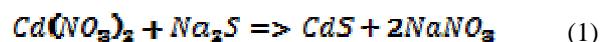
One of the most promising materials for the creation of hybrid structures is the methylene blue (MB) dye.

Properties of this dye allow the use of it for various applications, including chemical indicators, markers and spectral-sensitization systems for photovoltaic and photocatalysis of elements [7-10].

Acridine yellow (AY) dye is used as indicators in medicine, biology, microbiology, pharmaceuticals, for the detection of residual microfertility of drugs, for example, oxacillin-based antibiotics. In microbiology it is used as a mutagen when working with chromosomes. It is also a fluorescent dye and a local anti-inflammatory agent [11, 12].

I. Materials and methodology of the experiment

Investigated cadmium sulfide nanocrystals were obtained by chemical method from solutions of cadmium salts (cadmium nitrate) and sulfur (sulfide sulfur) in colloidal solution of gelatin. The formation of CdS particles occurs as a result of the exchange reaction:



Dyes: methylene blue and acridine yellow of different concentrations were added to the colloidal solution of cadmium sulfide after the synthesis process.

Optical absorption spectra were measured on a spectrophotometer SF-26 in the wavelength range from

320 nm to 600 nm. To reduce the error associated with the effect of light scattering, in the short-wave region (320-360 nm), the USF-2 light filter was used, which drove out the visible region of the spectrum. Measurement error did not exceed $\pm 01\%$. The luminescence was excited by a pulsed laser LCS-DTL-374QT with a wavelength of 355 nm. Laser power is 35 mW.

The average particle radius was estimated from the spectra of optical absorption.

According to the theory of interband absorption [13], the effective band gap of the nanocrystals E_g^* (the energy of the transition between the upper hole and the lower electron levels) increases with a decrease in the radius of the particles by law:

$$\hbar\omega = E_{lg}^* + E_{ln}^{\uparrow}(e, h), \quad (2)$$

where E_g^* is the optical width of the banned zone of a bulk crystal; $E_{ln}^{e,h}$ is the energy of dimensional quantization, inversely proportional to the square of the radius of the nanoparticle; l and n are the orbital and main quantum numbers. The dimensional quantization energy is defined as the difference between the effective width of the forbidden band of the nanocrystal and the single crystal. It can be calculated by the formula (2):

$$E_{ln}^{\uparrow}(e, h) = (\hbar^2 \varphi_{ln}^2) / (2m_{e,h} r^2), \quad (3)$$

where $m_{e,h}$ are the electrons and holes of the exciting masses; r - mean radius of nanoparticle; φ_l, n are the roots of the Bessel functions (for quantum numbers $l = 0$ and $n = 1$, $\varphi_{01} = 3.142$).

II. Research results and their discussion

By using formula 3, the size of the CdS QD was determined, which is equal to 3.1 ± 0.3 nm. The obtained QDs have a wide luminescence band localized in $\lambda_{\max} = 620$ nm.

Figure 1 shows absorption spectra of nanocrystals (NC) CdS (curve 1), dye MB of different concentrations (curves 2-4) and dye AY (curve 5). Dye MB has a wide absorption band in the range from 450 nm to 700 nm, and acridine yellow - from 320 nm to 500 nm. The presented graph illustrates absorption spectra of dyes at various concentrations.

On the spectrum of absorption of dye MB there is a structural band consisting of two components, which according to the literature data [14] correspond to different states: the molecular ($\lambda = 630$ nm) and aggregated ($\lambda = 580$ nm) (curve 2). The long-wave part corresponds to the molecular form, and the short-wavelength is aggregated (dimers). As the concentration of the dye increases, the intensity in the aggregated state increases (curves 3, 4).

The absorption spectrum of the QD CdS (curve 1) coincides with the absorption spectrum of the dye AY (curve 5) and does not coincide with the absorption spectrum of the dye MB (curves 2-4).

The absorption spectrum of the QD system CdS-dye MB is shown in Figure 2. The short-wave spectrum of the spectrum coincides with the absorption curve of NC

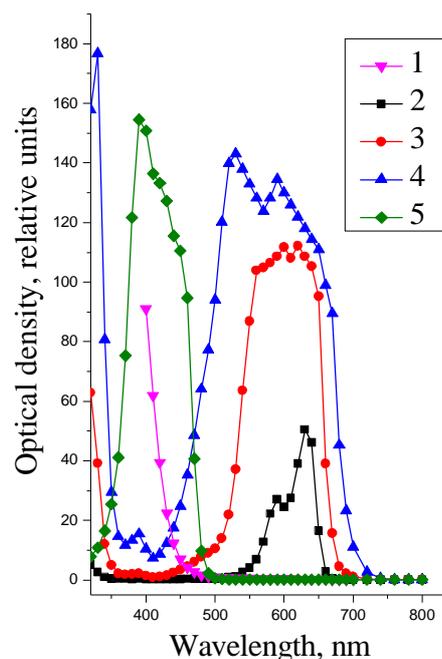


Fig. 1. Absorption spectra of NC CdS (1) and dye MB concentration $5 \cdot 10^{-6}$ M (2); $27 \cdot 10^{-6}$ M (3); $80 \cdot 10^{-6}$ M (4) dye AY concentration $37 \cdot 10^{-6}$ M (5).

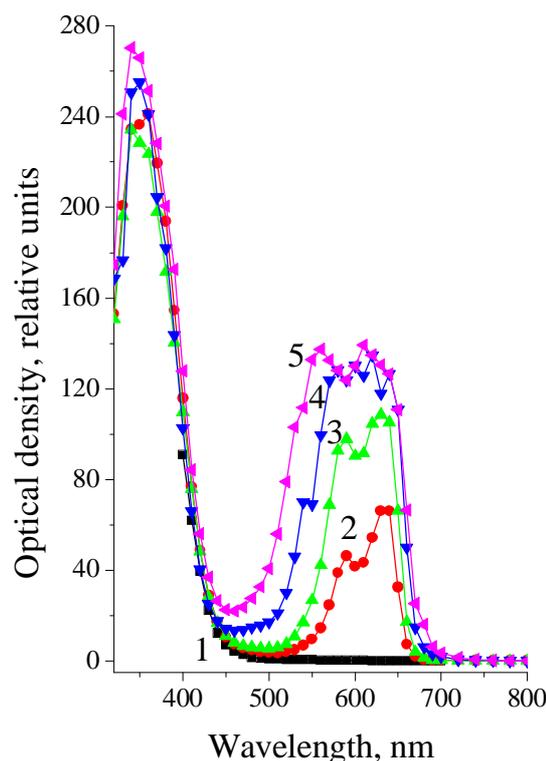


Fig. 2. Absorption spectra of NC CdS (1) and NC CdS with dye MB of different concentrations: $5 \cdot 10^{-6}$ M (2); $11 \cdot 10^{-6}$ M (3); $16 \cdot 10^{-6}$ M (4); $27 \cdot 10^{-6}$ M (5).

CdS, and the long-wavelength is the absorption spectrum of the dye. Note that in the region of 355 nm (wavelength of the exciting laser), the dye does not absorb and this wavelength is the exciting light only for NC CdS. This remark is significant in explaining the following results.

The spectra of the luminescence of CdS (Fig. 3, curve 1) have an intense luminescence with a maximum

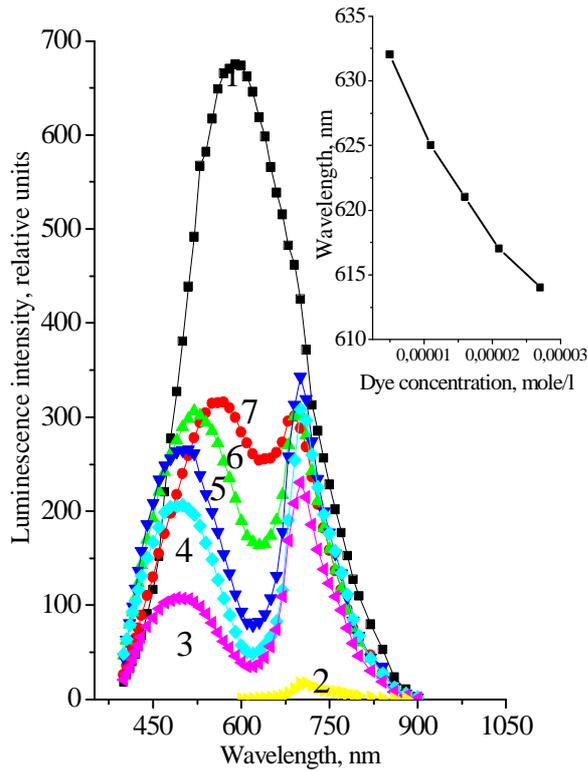


Fig. 3. Spectra of luminescence NC CdS (1), dye MB concentrations $5 \cdot 10^{-6}$ M (2) and NC CdS with dye MB, concentration: $27 \cdot 10^{-6}$ M (3); $21 \cdot 10^{-6}$ M (4); $16 \cdot 10^{-6}$ M (5); $11 \cdot 10^{-6}$ M (6); $5 \cdot 10^{-6}$ M (7). On the tab: Dependence of the minimum position on the luminescence spectrum of the nanosystem of the CdS-dye on the concentration of the dye.

$\lambda = 600$ nm. When the colorant MB is added to the colloidal solution with the lowest concentration of 5×10^{-6} M (Fig. 3 of curve 7), the intensity of the dye increases 20 times with respect to the dye in the initial state (curve 2). In this case, the luminescence contour undergoes significant changes, namely, the luminescence of the long-wavelength part of the photoluminescence of CdS NC disappears and a narrower strip of dye with a maximum of 700 nm appears, the intensity of which depends on the concentration of the dye.

The dye absorbs in the region from 550 nm to 650 nm, and emits in the region of large wavelengths. Characteristically, in the region of absorption of dye, the luminescence of CdS NC is absent. The whole spectrum consists of two bands, namely, the minimum of the system's QD system, the CdS-dye MB corresponds to the maximum luminescence of the CdS QD.

Changing the luminescence intensity in the minimum luminescence of the hetero system of QD CdS-dye MB is shown in the insert to Figure 3. The intensity of the luminescence of NC CdS with a dye in the region of 620 nm with an increase in the concentration of the dye decreases.

As the concentration of the dye increases, the width of the area of its absorption increases (Fig. 3). The luminescence of NC CdS in the corresponding absorption region of the dye decreases (Fig. 3, curves 3-7). The

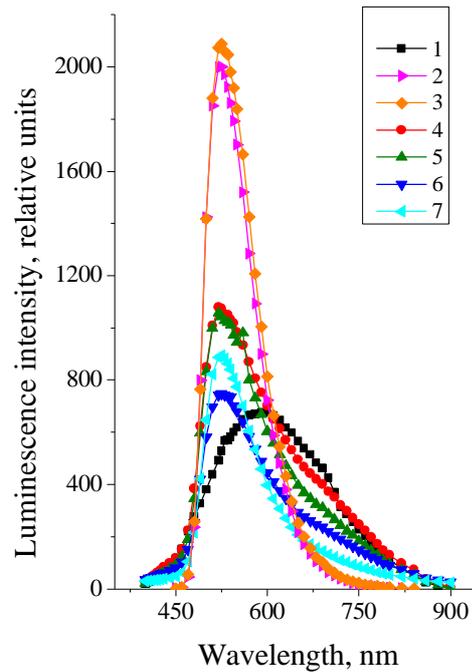


Fig. 4. The spectra of the luminescence of the CdS (1), the dye AY concentrations: $37 \cdot 10^{-6}$ M (2), $183 \cdot 10^{-6}$ M (3), and the CdS NC with a dye AY concentrations: $7 \cdot 10^{-6}$ M (4), $22 \cdot 10^{-6}$ M (5), $37 \cdot 10^{-6}$ M (6), $183 \cdot 10^{-6}$ M (7).

pattern we observe can be explained from the point of view of the processes of absorption in this structure and the transfer of the luminescence energy of the NC CdS to the dye in the region where it absorbs [15-18]. To confirm this mechanism, a similar experiment with a dye having an absorption band in the short-wave region was conducted.

Absorption spectra and dye AY, and NC CdS are in the same interval of wavelengths (Fig. 1). Figure 4 shows the spectra of the luminescence of the CdS (curve 1), the dye (curves 2,3) and the CdS with the dye (curves 4-7). It is seen that in this structure energy absorption by the dye occurs, which corresponds to the short-wave part of the luminescence band CdS. As a result, luminescence of the dye is observed in this area. At the same time, in the long-wavelength region, the luminescence spectrum of NC CdS remains unchanged. This is especially noticeable in solutions containing different concentrations of the dye, namely, when the dye concentration increases, the contribution of luminescence of NC cadmium sulfide to the stimulation of luminescence of the dye increases. This is also confirmed by the normalized spectra of these curves (Figure 5).

By deducting curve 2 from curve 3 (Fig. 5), a luminescence spectrum of cadmium sulfide was obtained, which was formed as a result of the absorption of part of the energy of its luminescence by a dye (Figure 5, insert).

It is observed that the luminescence of the short-wave part is absent, since this energy was absorbed by a dye.

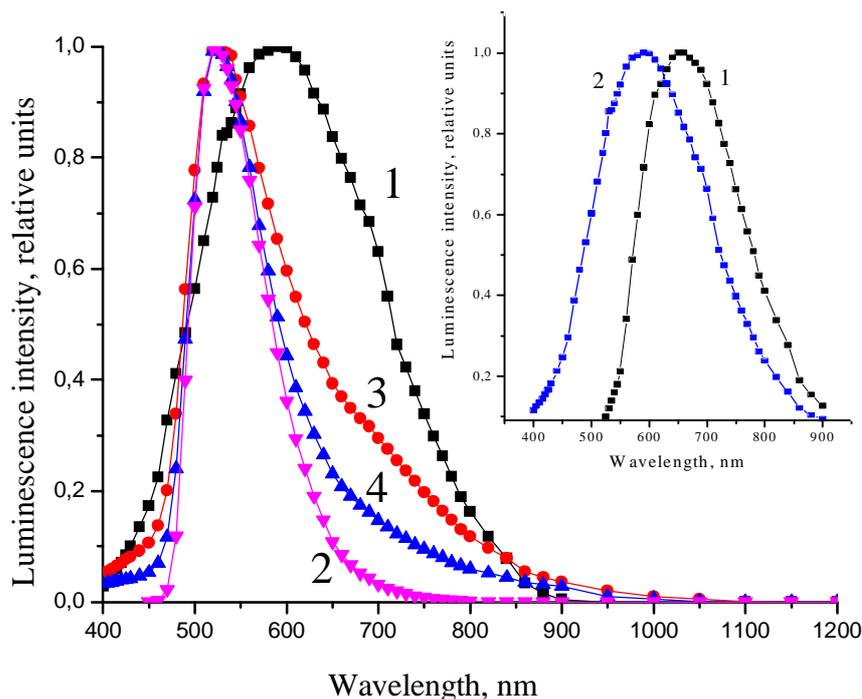


Fig. 5. Normed spectra of luminescence of NC CdS (1), dye AY concentration $37 \cdot 10^{-6}$ M (2) and NC CdS with dye AY, concentration: $37 \cdot 10^{-6}$ M (3), $183 \cdot 10^{-6}$ M (4) Insert: CdS Luminescence spectra: without dye (1), and with dye (2). The spectrum of photoluminescence (2) was obtained by subtracting curve 2 from curve 3.

Conclusions

As a result of the investigation the influence of dyes on the MB and AY on the QD CdS luminescence, the transformation of the luminescence QD spectrum was detected. The spectrum of the luminescence of the heterosystem QD CdS-dye depends on the absorption region of the dye. The spectrum of the luminescence of the quantum dots is shifted to the red region by the introducing into colloidal solution of the MB dye and in a case of the insertion of AY the spectrum is shifted into the blue one.

It was shown that luminescence of dyes is excited by the light of luminescence of QD CdS, and with increasing concentration of dyes, the contribution of luminescence of QD CdS to the stimulation of

luminescence of dyes increases.

The mechanism that causes the transformation of the contour of the photoluminescence spectrum of QD CdS is associated with the processes of transferring energy from the CdS to the colorants.

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- [1] Zh. Han, N. Wang, H. Zhang, X. Yang, Journal of Applied Spectroscopy 83(6), 1007 (2017).
- [2] Herman Sander Mansur and Alexandra Ancelmo Piscitelli Mansur, J. Mater. Chem. 22, 9006 (2012).
- [3] Fábio P Ramanery, Alexandra AP Mansur, and Herman S Mansur. One-step colloidal synthesis of biocompatible water-soluble ZnS quantum dot/chitosan nanoconjugates Nanoscale Res Lett. 8(1), 512 (2013).
- [4] A. Moulick, V. Milosavljevic, J. Vlachova, R. Podgajny, D. Hynek, P. Kopel, V. Adam, International Journal of Nanomedicine. 12, 1277 (2017).
- [5] J. Reyes-Esparza, A. Martínez-Mena, I. Gutiérrez-Sancha, P. Rodríguez-Fragoso, G. Gonzalez de la Cruz, R. Mondragón, L. Rodríguez-Fragoso. J Nanobiotechnology. 13, 83 (2015).
- [6] S. Zhang, R. Geryak, J. Geldmeier, S. Kim, and Vladimir V. Tsukruk. Chem. Rev. (2017).
- [7] S. Jockusch, D. Lee, Nicholas J. Turro, and Edward F. Leonard. Proc. Natl. Acad. Sci. USA. 93, 7446 (1996).

- [8] D. Gabrielli, E. Belisle, D. Severino, Alicia J Kowaltowski, Mauricio S Baptista. Photochem Photobiol. 79(3), 227 (2004).
- [9] M.S. Smirnov, O.V.Ovchinnikov, T.S.Shatskikh, A.G.Vitukhnovsky, S.A.Ambrozevich, A.S.Perepelitsa. Journal of Luminescence. 156, 212 (2014).
- [10] E M Tuite, J M Kelly. J Photochem Photobiol. 21 (2-3), 103 (1993).
- [11] N.O. Geokchian, A.A.Egiiazarin. Herald of Surgery of Armenia named after G. S. Tamazyan. 1 (66), 30 (2009).
- [12] N.O. Geokchian. Herald of Surgery of Armenia. 2(71), 109 (2011).
- [13] Al.L. Efros, A. L. Efros. P. and tech semiconductors. 16(7), 1209 (1982).
- [14] B.I. Shapiro. The success of chemistry.75 (5), 484 (2006).
- [15] V.L. Ermolaev, E. B. Sveshnikov, E. N. Bodunov. Advances in physical sciences.166 (3), 279 (1996).
- [16] V.N. Breger, Yu. L. Kolesnikov, A. V. Sečkarev. Optics and spectroscopy.78 (2), 249 (1995).
- [17] A.G. Vitushnovsky, A. A. Vashchenko, V. S. Lebedev, R. B. Vasiliev, P. N. Brunkov, D. N. Bychkovsky. Physics and technology of semiconductors. 47 (7), 962 (2013).
- [18] I.L. Medintz, A. R. Clapp, J. S. Melinger, J. R. Deschamps, H. Mattoussi. A. Reagentless, Advanced materials 17(20), 2450 (2005).

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Вплив органічних молекул на люмінісцентні властивості композитів на основі квантових точок CdS

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Досліджено вплив барвників метиленового блакитного (МБ) і акридинового жовтого (АЖ) на спектри люмінесценції композитів барвників з квантовими точками (КТ) CdS. Показано, що спектр люмінесценції гетеросистеми нанокристалів (НК) CdS - барвник залежить від області поглинання барвника. При введенні в колоїдний розчин МБ барвника спектр люмінесценції квантових точок зміщується в червону область, а при введенні АЖ - в блакитну. Отримані результати пояснюються з точки зору передачі енергії від квантових точок CdS до барвників за механізмом Ферстера.

Ключові слова: квантова точка, барвник, люмінесценція, механізм передачі енергії.