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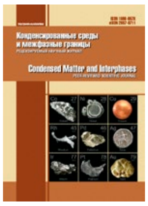

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Trap state and exciton luminescence of colloidal PbS quantum dots coated with thioglycolic acid molecules

I. G. Grevtseva, M. S. Smirnov, K. S. Chirkov, O. V. Ovchinnikov✉

Voronezh State University,
1 Universitetskaya pl., Voronezh 394018, Russian Federation

Abstract

This work presents the results of studying the IR luminescence of colloid PbS quantum dots coated with molecules of thioglycolic acid.

Luminescence of the sample was recorded using the InGaAs image sensor PDF 10C/M (ThorlabsInc., USA) and ~~a~~ diffraction monochromator with 600 mm^{-1} grating. To study the temperature dependence of luminescence, the sample was cooled in a nitrogen cryostat down to 80 K. A redistribution of the luminescence intensity between two peaks (1100 and 1280 nm) was identified upon a decrease in temperature. It was shown that an exciton absorption peak was present in the excitation spectrum for the short-wave luminescence peak, and the Stokes shift was $\Delta E_{\text{stokes}} \sim 0.1$ eV. On the contrary, the exciton peak was absent in the luminescence excitation spectrum of the long-wave band, and its red boundary was shifted towards the short-wave region, that provided the Stokes shift of more than 0.3 eV.

It was concluded that the short-wave luminescence band appeared as a result of the radiative annihilation of an exciton, while the long-wave band appeared due to the recombination of charge carriers at trap states. Trap state luminescence was effectively excited upon direct absorption of the radiation by the luminescence centre. A three-level diagram was suggested that determined the IR luminescence of colloid PbS quantum dots coated with thioglycolic acid molecules.

Keywords: Lead sulphide quantum dots, Luminescence spectra, Excitation spectra

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✉ Oleg V. Ovchinnikov, e-mail: ovchinnikov_o_v@rambler.ru

1. Introduction

Semiconductor colloid quantum nanocrystals (quantum dots or QDs) attract interest due to their wide range of potential application in various optoelectronic devices and systems. QDs can be used in optic sensors and laser emitters and as non-linear media for controlling intensity, radiation phase, etc. [1–4]. It is possible to use QDs in various devices as their spectral and transport properties can be easily adjusted due to the quantum size effect.

A detailed understanding of the photoprocesses regulerities that determine the size-dependent spectral-luminescent properties is required for the practical application of QDs. In case of non-stoichiometric compounds, photoprocesses are also significantly complicated by the participation of Defect trap states. PbS is one of the typical representatives of non-stoichiometric semiconductors [5]. The increased interest in PbS is associated with the possibility of its use in the IR range as the band gap of a bulk crystal is 0.41 eV [6] and the exciton Bohr radius is approximately 20 nm. The absorption bands from IR to the visible range can be controlled by varying the crystal sizes in the range of 1–20 nm due to the quantum size effect [7–13].

Controlling the position of luminescence peaks is an individual large task. Together with a change in the energy structure of exciton states due to variation in the QD size, there is also a possibility to obtain new luminescence bands determined by optical transitions on trap states of charge carriers [15–17].

Still, in each specific case it is necessary to establish the photoprocesses regularities and luminescence mechanisms for different types of semiconductors. At the present time for PbS QDs, the observed experimental regularities turn out to be very contradictory [7–13].

In [9], it was shown for PbS QDs dispersed in polyvinyl films that upon a temperature increase from 10 to 250 K the width of the effective band gap decreased ($\Delta E_g/\Delta T = -1.1 \cdot 10^{-4}$ eV/K). On the contrary, the width of the band gap increased for massive PbS upon a temperature increase ($\Delta E_g/\Delta T = +4.7 \cdot 10^{-4}$ eV/K) [18]. Based on the temperature dependences, the complex band in the QD luminescence spectra was decomposed into three peaks [9] with the Stokes shift (0.47, 0.25, and 0.17 eV). All three peaks were correlated with the recombination of charge carriers on trap states. However, in [7,8,12,13,19], an exciton luminescence mechanism was assumed for luminescence peaks with a Stokes shift regarding the exciton absorption peak in the range from 0 to 0.6 eV.

In [10], two luminescence peaks were discovered for PbS QD films coated with ethanethiol. Based on the data of femtosecond transient absorption spectroscopy, the process of thermal release of localized charge carriers was shown. The increase in the short-wave luminescence peak and decrease in the long-wave peak were observed under an increase in temperature. The increase in the short-wave luminescence peak and decrease in the long-wave peak were observed under an increase in temperature. It was concluded that the short-wave luminescence peak corresponded to radiative exciton annihilation, while the long-wave peak corresponded to the recombination on trap states.

In [20], the complex luminescence band for PbS QDs was also represented by the total of three individual components. Based on the analysis of the data of time-resolved luminescence, it was concluded that the short-wave luminescence peak was determined by the radiative exciton annihilation. As for the other two peaks, the authors associated them with phonon repetitions, although there was a strong difference in the luminescence kinetics of all three bands.

Therefore, the existing experimental data on the regularities of the PbS QD luminescence are very contradictory.

In this work we present the results of studies of the luminescence regularities of colloidal PbS QDs coated with thioglycolic acid molecules (PbS/TGA QDs).

2. Experimental

1.1. Synthesis method

Colloidal PbS/TGA QDs were synthesised in water using thioglycolic acid (TGA) molecules as a passivator of the QD surface. The synthesis method was based on the techniques that we used previously to obtain colloidal solutions of silver and cadmium sulphide QDs [14, 17].

The synthesis of PbS QDs was based on the reaction of substitution of thioglycolic acid molecules for sulphur atoms in the Pb:TGA precursor. At first, 1.5 mmol of $Pb(NO_3)_2$ were dissolved in 50 ml of distilled water, and thioglycolic acid (3 mmol) was added. After that, the pH level was increased up to 9 by the addition of NaOH (1 M), which allowed obtaining the $Pb(SCH_2COONa)_2$ precursor. The addition of an aqueous solution of Na_2S (0.85 mmol) was accompanied by a change in colour to brown, which indicated the formation of PbS/TGA QDs. The obtained solution of colloidal QDs was precipitated with acetone (which was added by volume to a concentration of 50%) and centrifugation. The precipitate was gathered and dissolved again in distilled water. The process of purification was repeated twice. Thus, the studied samples were a colloidal solution of PbS/TGA QDs in water.

2.2. Experimental techniques

Structural studies of the sample were conducted using transmission electron spectroscopy (TEM) with a Libra 120 microscope (CarlZeiss, Germany) and a digital analysis of TEM images and X-ray diffraction. The size dispersion of QDs was determined in the sample using TEM images.

Absorption spectra were recorded on a USB2000+ spectrometer (Ocean optics) with a USB-DT radiation source (Ocean optics). Luminescence spectra in the IR region were recorded on a PDF 10C/M image sensor (ThorlabsInc., USA) with the built-in amplifier and ~~a~~ diffraction monochromator with a 600 mm^{-1} grating. The luminescence spectra were corrected for the spectral characteristics of the devices which was measured using a reference incandescent tungsten lamp with a known colour temperature.

We used the 400 W incandescent lamp and ~~a~~ second monochromator with a 1200 mm^{-1} grating in order to obtain the luminescence excitation spectra, which resulted in an excitation region from 500 to 1300 nm.

We placed the sample in a nitric cryostat and cooled it down to 80 K in order to record the luminescence spectra of the studied sample at low temperatures.

3. Results and discussion

Figure 1a shows a TEM image of the studied samples of PbS/TGA QDs with a histogram of the QD size distribution. It can be seen that the suggested synthesis method allowed obtaining individual nanoparticles with an average size of about 3 nm. The size dispersion was approximately 25–30 %.

Figure 1b shows X-ray diffraction from a PbS QD sample for CuKα radiation with a 1.056 Å length, and there are well-distinguished reflections at 25.9°, 30.1°, and 43.05°, corresponding to the cubic modification of the PbS crystal. All

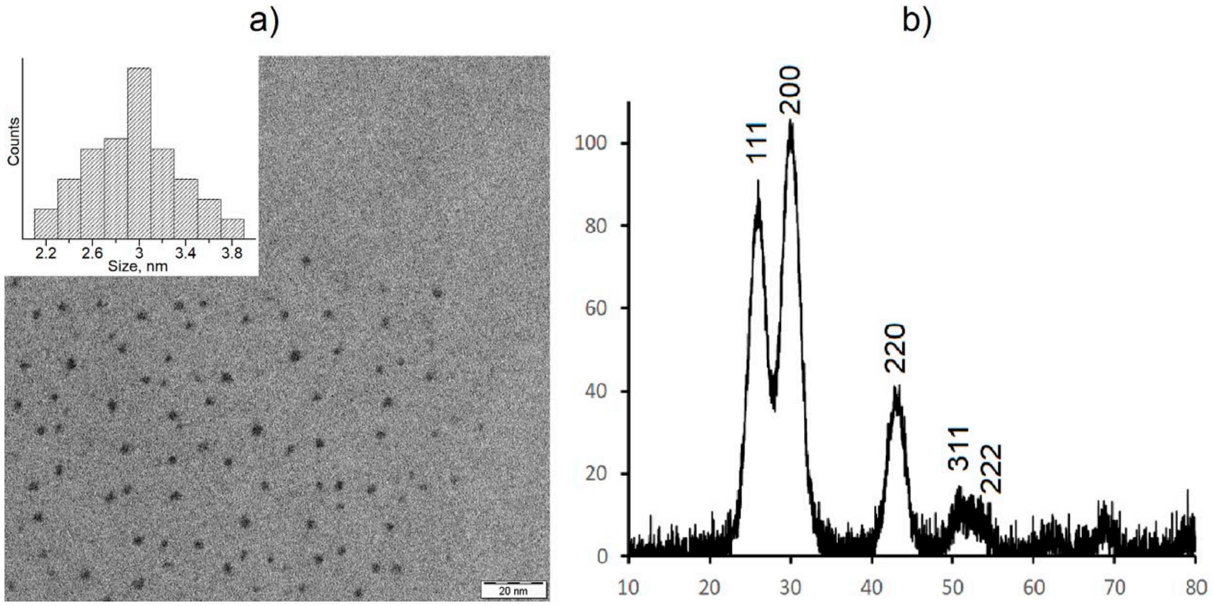

Fig. 1. TEM image of PbS/TGA QDs with size distribution histogram (a). X-ray diffraction from a sample (b)

reflections were significantly broadened. The size of the crystallites was assessed using the Scherrer equation:

$$d = \frac{0.9\lambda}{\beta\cos\theta}, \tag{1}$$

where d is the size, nm, λ is the wavelength of the X-ray emission 0.15405 nm, β is the width of the diffraction peak at half height (the (220) peak was used as it did not overlap with other reflections), θ is the Bragg angle. The size value was of about 3–3.5 nm, which correlated well with the TEM data. Therefore, the synthesized sample was a set of PbS nanocrystals with an average size of about 3 nm.

Figure 2 shows the optical absorption spectrum of PbS/TGA QDs. The edge of the absorption spectrum located in the region of about 1000 nm was shifted towards the short-wave region in relation to the absorption edge of bulk PbS (0.41 eV or 3025 nm), which indicated the quantum limitation of charge carriers. The exciton structure was absent for the absorption spectrum, which is typical for QDs from semiconductors with a high degree of non-stoichiometry [14]. In this case, the shape of the absorption spectrum can be determined not only by transitions between the quantum size states of the nanocrystal but also by transitions with the participation of trap states. A significant contribution to the absence of an exciton structure was also determined by the considerable size dispersion of QDs in the sample.

Intensive IR luminescence emerged upon the excitation with the wavelength of 462 nm, its spectrum is also presented in Fig. 2. The luminescence spectrum was not elementary and there were at least two peaks, a short-wave peak with the maximum of about 1100 nm and a long-wave peak with the maximum of about 1280 nm. The half width at half-maximum (HWHF) of both luminescence peaks was estimated to be within the range of 0.1–0.2 eV. Narrow luminescence peaks for QDs are usually attributed to radiative exciton annihilation, but luminescence peaks with a HWHF not more than 0.2 eV can also be some semiconductor compounds, even in case of trap-state luminescence [14]. In our case, the absence of an exciton structure in the absorption spectrum did not allow determining the Stokes shift for the identified luminescence peaks. To establish the luminescence mechanisms, we need to consider the luminescence excitation spectra.

As opposed to the absorption spectra that are determined by the absorption of each nanocrystal in the sample, only the QDs emitting in the wavelength of emission recording participate in the formation of the excitation spectra. This allowed achieving selectivity by the wavelength in the luminescence excitation spectra through a change in the wavelength of emission recording.

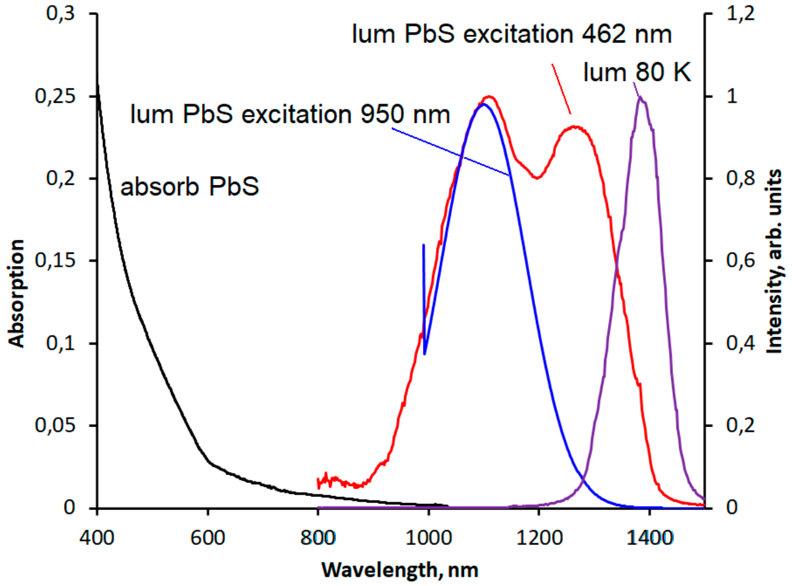

Fig. 2. Spectra of absorption and luminescence of colloidal solutions of PbS/TGA QDs in a quartz cuvette

Figure 3 presents the luminescence excitation spectra recorded at the peak of the observed bands. Narrow intense peaks in the region of 1100 and 1280 nm with a HWHF of approximately 15 nm were associated with the scattering of the excitation radiation, when its wavelength was the same as the wavelength of the luminescence recording. A specific feature was observed with a peak at 990 nm in the luminescence excitation spectrum in the short wavelength band (1100 nm). According to the position and shape of this peak, it was associated with absorption into the ground state of the exciton. In this case, the Stokes shift of the luminescence peak in relation to the exciton absorption peak was 0.125 eV. This value is typical for the PbS QDs exciton luminescence with an average size of about 3–3.5 nm. On the contrary, no exciton structure was found in the luminescence excitation spectrum with a peak at 1280 nm. The excitation band edge was located in the region of 950 nm while the Stokes shift value increased up to 0.33 eV. This allowed associating the long-wave luminescence band with the radiative recombination of charge carriers on trap states. It should be noted that the excitation of the recombination band from the exciton absorption peak was not effective enough (the exciton absorption peak was absent from the excitation spectrum). Indeed, the intensity of the long-wave band was significantly lower as compared to the short-wave band upon excitation with a wavelength of 950 nm (Fig. 2). The strong absorption by trap states was also shown in [10] as compared to its own exciton absorption for PbS QDs.

If the suggested luminescence mechanisms of colloidal PbS/TGA QDs (recombination and exciton bands) are correct, and both luminescence peaks belong to each QD in the sample, not to individual nanocrystals, there must be some relationship between the intensity of the luminescence bands. And in fact, there is. When the PbS/TGA colloidal QD sample was cooled down to 80 K, the luminescence band with a peak at 1100 nm disappeared, and the radiation in the long-wave band became more intense (Fig. 2). As it cooled down, the long-wave luminescence peak gradually shifted towards the long-wave region from 1280 to 1380 nm, by 0.07 eV.

The dependence of the relative intensity of the luminescence bands on temperature showed that both bands belonged to each nanocrystal in the sample and allowed creating a diagram of energy levels and the transitions between them (Fig. 4). The diagram includes a non-excited

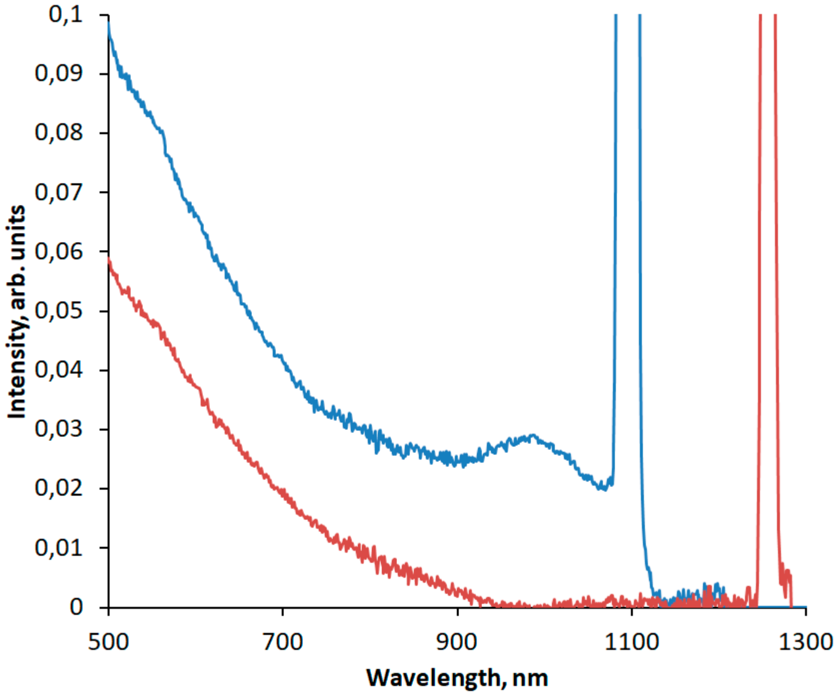

Fig. 3. Luminescence excitation spectra

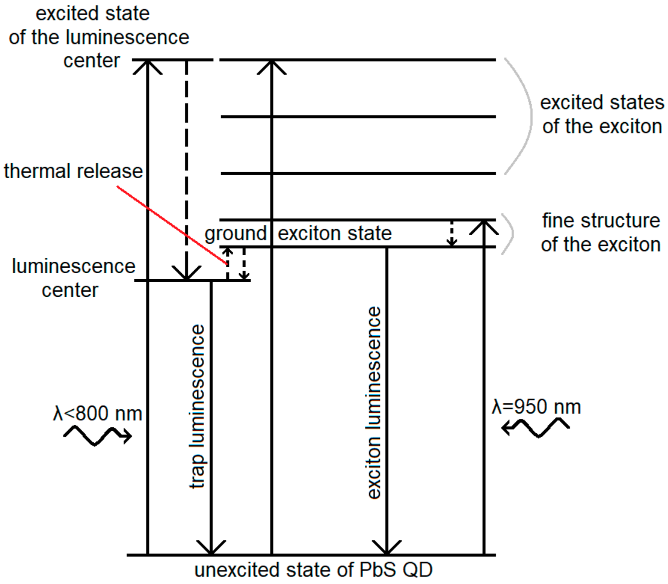

Fig. 4. Diagram of energy transitions in PbS/TGA QDs

state and several excited states of the exciton determine by the ground and ~~the~~ excited state of the electron and ~~the~~ hole at the quantum size levels of the nanocrystal. There were also several levels of the excited state of the trap state luminescence centre.

The observation of two peaks in the luminescence spectrum at room temperature can be explained by the fact that charge carriers are mainly captured by the excited state of the trap when QDs are excited by radiation with a wavelength of 462 nm. After that, charge carriers can move to the exciton level as a result of thermal activation. Therefore, charge carriers are able to recombine both from the trap and from the exciton levels. The thermal activation of the transition to the exciton level also explains the absence of an exciton peak in the spectrum upon cooling the sample down to a temperature of 80 K. When QDs are excited by radiation with a wavelength of 950 nm, the exciton is excited directly. In this case, the capture of charge carriers by the trap state luminescence centre was less efficient as compared to the radiative exciton annihilation, which can explain the weakening of the peak associated with the luminescence from the trap. Thermal excitation of charge carriers from the luminescence centre to the exciton state contributed to the increase in the population of the latter and the increase in the exciton luminescence with increasing temperature. Excitation of the exciton state with the lowest energy (the wavelength of about 950 nm) apparently corresponded to non-resonant low-efficiency excitation of the luminescence centre. The capture of charge carriers from the exciton state to the luminescence centre was also a slow process. The low capture rate contributed to the dominance of exciton luminescence upon direct excitation by radiation with a wavelength of 950 nm, which corresponded to the region of the exciton absorption peak (Fig. 3).

Therefore, the intense IR luminescence identified for PbS/TGA QDs in two bands corresponded to radiative exciton annihilation at 1100 nm and to recombination on trap states in the long-wave region.

4. Conclusions

In this work we presented new regularities in the IR luminescence of colloid quantum dots of lead sulphide coated with the molecules of thioglycolic acid. Two luminescence peaks with peaks at 1100 nm and 1280 nm were found. A temperature decrease down to 80 K was accompanied by the decrease in luminescence intensity in the short-wave band and simultaneous increase in the intensity of the long-wave luminescence peak. In addition, fundamental differences were found between the photoluminescence excitation spectra for two peaks. The exciton structure was present in the excitation spectrum of the short-wave luminescence peak while the Stokes shift was about 0.1 eV. On the contrary, no exciton structure was found in the excitation spectrum for the long-wave luminescence peak, while the Stokes shift in the luminescence peak in relation to the long-wave edge of the excitation spectrum was approximately 0.3 eV. It was concluded that the nature of the short-wave peak (1100 nm) was associated with the radiative exciton annihilation, and the long-wave peak emerged as a result of the recombination of charge carriers on trap states. We proposed an empirical diagram of photoprocesses that takes into account the thermal redistribution of the populations of the exciton state and trap state luminescence centre together with the special features of direct excitation of trap state luminescence.

Author contributions

I. G. Grevtseva – methodology development, text writing and editing. M. S. Smirnov – research concept, conducting research, review writing, and text editing. K. S. Chirkov – conducting research, review writing. O. V. Ovchinnikov – scientific supervision, research concept, methodology development, text writing, final conclusions.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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Information about the authors

Irina G. Grevtseva, Cand. Sci. (Phys.–Math.), Lecturer at the Department of Optics and Spectroscopy, Voronezh State University (Voronezh, Russian Federation).

https://orcid.org/0000-0002-1964-1233
grevtseva_ig@inbox.ru

Mikhail S. Smirnov, Dr. Sci. (Phys.–Math.), Associate Professor, Department of Optics and Spectroscopy, Voronezh State University (Voronezh, Russian Federation).

https://orcid.org/0000-0001-8765-0986
smirnov_m_s@mail.ru

Kirill S. Chirkov, postgraduate student, Department of Optics and Spectroscopy, Voronezh State University (Voronezh, Russian Federation).

https://orcid.org/0000-0003-0387-0733
kirill200598@mail.ru

Oleg V. Ovchinnikov, Dr. Sci. (Phys.–Math.), Professor at the Department of Optics and Spectroscopy, Voronezh State University (Voronezh, Russian Federation).

https://orcid.org/0000-0001-6032-9295
ovchinnikov_o_v@rambler.ru

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