TEMPERATURE DEPENDENCIES OF SPECTRAL AND KINETIC PROPERTIES OF PBS QD PHOTOLUMINESCENCE

Aleksandr P. LITVIN, Peter. S. PARFENOV, Elena V. USHAKOVA, Ana L. SIMÕES GAMBOA, Anatoly V. FEDOROV, Alexander V. BARANOV

ITMO University, 49 Kronverkskiy pr., Saint-Petersburg, 197101 Russia

Abstract

Temperature dependencies of spectral and kinetic photoluminescence properties of PbS QD of different sizes are investigated. We found up to 2 PL components in PbS QDs PL spectra and estimated corresponding temperature coefficients of PL peaks position shift. Obtained temperature coefficients and their size-dependencies differ for these PL components due to the different origin of corresponding electronic states. According to the spectral data, temperature dependence of PL lifetime was explained using the model with two emissive low energy electronic states. These states are coupled with nonradiative transitions of excitons; besides, efficiency of these transitions drastically depends on the temperature, leading to strong variation of PL lifetime with temperature.

Keywords: PbS, QDs, photoluminescence, temperature dependence

1. INTRODUCTION

Lead sulfide (PbS) quantum dots (QDs) have become important material for solar radiation harvesting [1–3]. In order to prognosticate operational parameters of PbS QDs based devices, electronic and optical properties of PbS QDs must be studied in details. For example, variation of spectral and kinetic properties of photoluminescence (PL) of PbS QDs with temperature has to be explored for further design of QD-based devices operating at reduced temperatures. Shift of the PL peak position and modification of the PL dynamics may change an efficiency of physical processes which are responsible for functioning of different appliances. For example, shift of PL band with temperature may significantly increase or decrease an efficiency of devices which exploit fluorescence resonance energy transfer (FRET) process, such as solar cells. Moreover, if PL and absorption bands have different coefficients of temperature shift, there is a possibility to tune a spectral overlap between them, varying temperature. Since different scientific groups reported contradictory data on temperature dependencies of PbS QD PL properties [4–9], thorough analysis of PL spectra and kinetics for QD of different sizes is required.

In the present work we performed steady-state and transient PL analysis of 3.2–6.9 nm QDs in a porous matrix in the temperature range of 77–300 K. We found up to 2 PL components in PbS QDs PL spectra for QDs of different size and estimated temperature coefficients of PL peak position shift for each one. According to the spectral data, temperature dependence of PL lifetime was explained using the model with two emissive low energy electronic states, coupled with nonradiative transitions of excitons.

2. METHODS

PbS QDs with diameters of 3.2–6.9 nm were synthesized using the method of hot injection [10]. QDs were stabilized with oleic acid and dissolved in tetrachloromethane (TCM). Synthesized QDs were infiltrated into the porous matrix as described in the Ref.[11]. Filter paper used as a porous matrix has adequate transparence in the near infrared region to conduct measurements of optical absorption and photoluminescence. Obtained samples were placed into the programmable cryostat (Linkam), which let us carry up the steady-state (15 mW of cw 633 He-Ne laser excitation) and transient (8 mW of 10 ns pulsed YLF:Nd^{3+} laser excitation at 4 kHz) PL experiments in the temperature range of 77–300 K. Recorded PL spectra were corrected using the spectral sensitivity curve, obtained by the calibration on an ideal black body

spectrum [12]. PL decay curves were averaged by 10^5 measurements to increase a signal/noise ratio [13, 14].

3. RESULTS AND DISCUSSION

3.1 PL spectra

PL spectra of PbS QDs embedded into the porous matrix demonstrate typical red shift of the peak position with temperature decrease (Fig.1). PL spectra of the smallest (3.2 and 3.6 nm) and the largest (6.9) QDs may be well fitted by one Gaussian, while fitting PL spectra of the QDs with intermediate sizes requires two Gaussians. This feature is caused by the existence of the peculiar radiative in-gap state in the low energy electronic structure of PbS QDs [10]. In case of the largest dots this effect does not manifest itself, and we can observe the PL from the fundamental 1s1s state only (PL1). Oppositely, in case of the smallest dots radiative recombination via the in-gap state (PL2) prevails in PL spectra. In case of intermediate dots both components contribute to the total PL spectrum. Besides, the high-energy component associated with the radiative recombination via the 1s1s state, while the low-energy one associated with the radiative recombination via the in-gap state

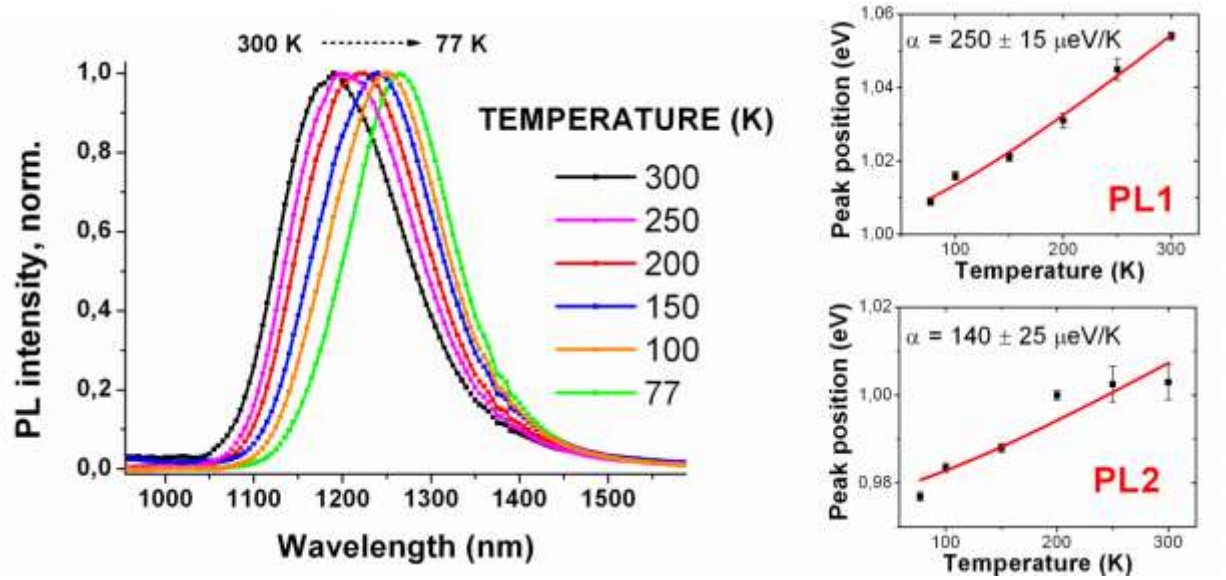

Fig.1. Typical red shift of the PL peak position with temperature decrease, recorded for 4.4 nm PbS QDs. PL spectrum composed of 2 PL components, Varshni fit and estimated temperature coefficients α of the PL peak position shift for PL1 and PL2 are shown in the right panel.

Using Varshni fit we can estimate temperature coefficients α of the PL peak position shift for both PL1 and PL2. We found that α is almost size-independent for PL2 with the value of ~125±15 μeV/K. This characteristic together with comparatively large FWHM evidences the defect-related origin of the in-gap state [10, 15, 16]. Oppositely, estimated for PL1 α depends on the QD size, namely, in increase with QD diameter decrease. This behavior is in contrast to that observed for PbS QD absorption [17]. This discrepancy may be caused by the splitting of the 1s1s state [18]. Thus, we have a possibility to tune a spectral overlap between absorption and PL spectra, varying temperature that may be used for optimization of FRET efficiency and FRET-based devices.

3.2 PL decay times

PL decay curves for the largest, 6.9 nm, QDs may be described using 2-exponential law in the whole temperature range. One component is short, 10–15 ns, and its decay time and amplitude do not depend on the temperature. This component presents in decay curves from all studied QDs and may be related to the

influence of laser excitation or photobleaching and would not be taken into consideration. Decay time of another component slightly increases from ~80 to ~100 ns with temperature decrease from 300 to 77 K due to the electron-photon interaction weakening. One-exponentional decay law indicates that only recombination via fundamental electronic state takes place in case of 6.9 nm QDs, that corresponds to the spectral data.

For 3.2 nm QDs beside the one invariable short component we can distinguish two different variable components. Decay time of the short one increases from 160 to 240 ns, while decay time of the long one increases from 1.5 to 2.1 μs with temperature decrease. An appearance of the component with very long decay time relates to the presence of long-lived in-gap state [10].

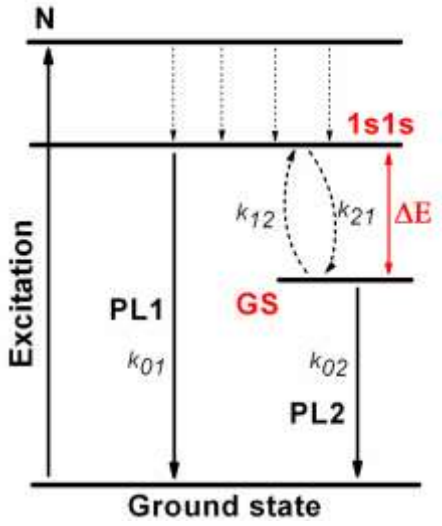

Fig. 2. The scheme of energy relaxation in intermediate -sized PbS QDs: PL1 relates to the 1s1s state and PL2 relates to the in-gap state (GS). Two these radiative states are separated by the *ΔE* energy gap and are coupled by nonradiative transitions k_{21} and k_{12}. PL1 and PL2 bands are characterized by recombination rates k_{01} and k_{02}, respectively.

We can distinguish up to 2 PL components in PL spectra for QDs of different sizes, so we can consider a simple energy scheme with two radiative levels (see Fig.2) in order to analyze the PL decay. These levels relate to the fundamental 1s1s and the in-gap state, respectively, and are coupled with nonradiative transitions of excitons with rates k_{12} and k_{21} [10, 19]. Using formalism of rate equations for states population we can find that PL1 and PL2 may be described as [20]:

$$PL_{1,2} = A_{1,2}e^{-\frac{t}{\tau+}} + B_{1,2}e^{-\frac{t}{\tau-}}, \quad (1)$$

where $A_{1,2}$ and $B_{1,2}$ are time-independent coefficients and $\tau^{\pm}$ is defined as:

$$\tau^{\pm} = 2\,[\,k_{01} + k_{02} \pm \sqrt{(k_{01} - k_{02})^2 + 4k_{21}k_{12}}\,]^{-1}, \quad (2)$$

where k_{01} and k_{02} include initial radiative and nonradiative recombination rates which characterize PL1 and PL2, respectively. One can see that: 1) for all QDs with the in-gap state we expect 2-exponentional decay law; 2) in such systems relaxation dynamics from each state is determined by relaxation rates from both states and by rates of nonradiative transitions between them. Hence, a rate of inverse transition from lower to upper state k_{12} will mainly govern the temperature dependence of relaxation dynamics for QDs of different sizes, because k_{12} drastically depends on temperature (see Fig.3) and may be expressed as:

$$k_{12} = k_{21}\exp(-\Delta E / k_B T)\,, \tag{3}$$

where ΔE is an energy gap between 1s1s and in-gap states, and k_B is a Boltzmann constant.

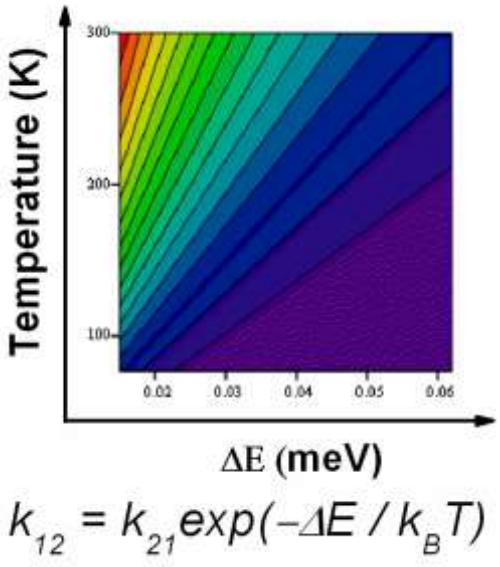

Fig. 3. Calculated rate k_{12} as a function of the energy gap (ΔE) and temperature (T).

Due to the fact that k_{12} depends also on the energy gap between two radiative states, i.e. QD size, we expect changes in size dependence of energy relaxation rates with temperature. Indeed, threshold-like PL decay time size-dependence obtained in Ref.[10] will modify with temperature decrease, namely, a threshold will shift to larger QDs (lower ΔE) as shown in the Fig.4. (calculated using data from Ref.[10]).

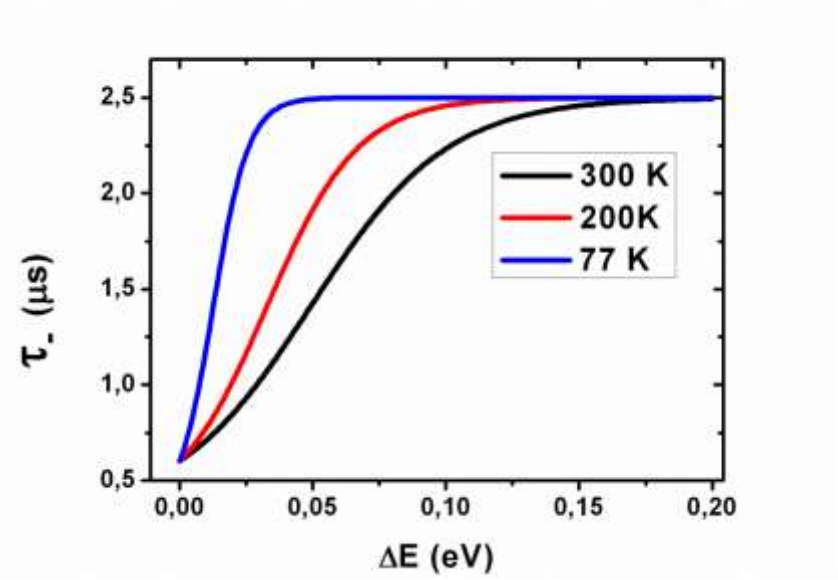

Fig. 4. Calculated temperature variation of the threshold-like PL decay time size-dependence.

Validity of the proposed model was checked on the example of temperature dependence of relaxation dynamics for 4.4 nm PbS QDs. In these QDs decay time of the fast component rises from 78±2 to 100±4 ns and decay time of the slow component rises from 315±5 to 590±10 ns when temperature decreases from 300 to 77 K. ΔE here decreases from 51 to 32 meV with temperature due to the different values α for PL1 and PL2 bands. An analysis of the proposed model shows that τ^+ slightly depends on temperature and is determined mainly by faster rate k_{01}, but τ^- varies in a wide range. From the data for 6.9 nm QDs we can estimate $k_{01}=1.2\times10^7\ s^{-1}$ to model τ^- in 4.4 nm QDs. The result of the fit is shown in the Fig.5. One can see that calculated τ^- may describe well decay constant of the slow component. At the same time τ^+ gives only ~55–57 ns which is less than 78–100 ns, obtained for the fast component in the experiment, which is shown in the inset to the Fig.5. We should appreciate that such approach gives rather rough quantitative estimation due to several reasons. First of all, k_{01} for 4.4 nm QDs, actually, differs from such for 6.9 nm QDs, used for fit. At the same time we do not have any reliable data on the rates k_{02} and k_{21} to adjust k_{01}. Secondly, such approach does not take into account the dependence of initial values of k_{02} and k_{21} on the temperature. In particular, for 6.9 nm QDs weakening of electron-photon interaction leads to increase of decay times from ~80 to ~100 ns. This is similar to that observed for τ^+ for 4.4 nm QDs and which has not been taken into account in rate equations for states population. With these stipulations, formalism of rate equations and proposed scheme of energy structure give tolerable quality description of the temperature dependence of relaxation dynamics in PbS QDs with the in-gap state.

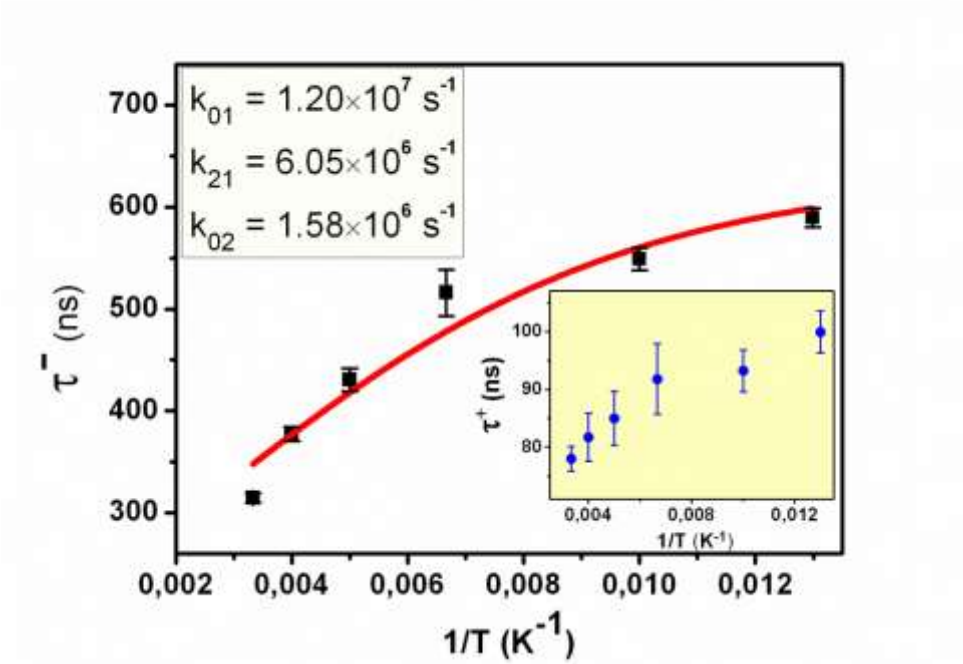

Fig.5. Measured and calculated τ^- for 4.4 nm PbS QDs. Inset – measured τ^+ for 4.4 nm.

CONCLUSION

In the present work we performed steady-state and transient PL analysis of 3.2–6.9 nm QDs in a porous matrix in the temperature range of 77–300 K. We found up to 2 PL components in PbS QDs PL spectra for QDs of different size and estimated temperature coefficients of PL peak position shift for each one. Obtained temperature coefficients and their size-dependencies differ for these PL components due to the different origin of corresponding electronic states. Surface defects related in-gap state possesses size-independent temperature coefficient α, while α for 1s1s radiative relaxation increase with QD diameter decrease. According to the spectral data, temperature dependence of PL lifetime was explained using the model with two emissive low energy electronic states, coupled with nonradiative transitions of excitons. Rates of these

transitions drastically depend on the temperature and the energy gap between radiative states, leading to strong variation of PL lifetime and PL lifetime size-dependence with temperature. The proposed model was checked on the example of temperature dependence of relaxation dynamics for 4.4 nm PbS QDs. The analysis shows that formalism of rate equations and proposed scheme of energy structure give tolerable quality description of the temperature dependence of relaxation dynamics in PbS QDs with the in-gap state.

ACKNOWLEDGMENT

This work was performed in the framework of the government assignment No. 3.109.2014/K of the Ministry of Education and Science of the Russian Federation. A.P.L and E.V.U. thank the Ministry of Education and Science of the Russian Federation for support through the scholarships of the President of the Russian Federation for Young Scientists and Graduate students (2013–2015).

LITERATURE

[1] JUMABEKOV, A., DESCHLER, F., BO, D., PETER, L., FELDMANN, J., and BEIN, T. Quantum-Dot-Sensitized Solar Cells with Water-Soluble and Air- Stable PbS Quantum Dots. *J. Phys. Chem. C*. 2014, vol. 118, pp. 5142–5149.

[2] CHANG, L., LUNT, R., BROWN, P., BULOVIĆ, V., and BAWENDI, M. Low-temperature solution-processed solar cells based on PbS colloidal quantum dot/CdS heterojunctions. *Nano letters*. 2013, vol. 13, no. 3, pp. 994–9.

[3] GÜNES, S, FRITZ, K., NEUGEBAUER, H., SARICIFTCI, N., KUMAR, S., and SCHOLES, G.. Hybrid solar cells using PbS nanoparticles. *Solar Energy Materials and Solar Cells*. 2007, vol. 91, no. 5, pp. 420–423

[4] GAPONENKO, M, LUTICH, A., TOLSTIK, N., ONUSHCHENKO, A., MALYAREVICH, A., PETROV, E., and YUMASHEV, K. Temperature-dependent photoluminescence of PbS quantum dots in glass: Evidence of exciton state splitting and carrier trapping. *Physical Review B*. 2010, vol. 82, no. 12, p. 125320

[5] YUE, F., TOMM, J., and KRUSCHKE, D. Spontaneous and stimulated emission dynamics of PbS quantum dots in a glass matrix. *Physical Review B*. 2013, vol. 87, no. 19, p. 195314

[6] LEWIS, J., WU, S., and JIANG, X. Unconventional gap state of trapped exciton in lead sulfide quantum dots. *Nanotechnology*. 2010, vol. 21, no. 45, p. 455402

[7] PONS, T., MEDINTZ, I., SYKORA, M., and MATTOUSSI, H.. Spectrally resolved energy transfer using quantum dot donors: Ensemble and single-molecule photoluminescence studies. *Physical Review B*. 2006, vol. 73, no. 24, p. 245302

[8] ULLRICH, B., WANG, J., and BROWN, G.. Analysis of thermal band gap variations of PbS quantum dots by Fourier transform transmission and emission spectroscopy. *Applied Physics Letters*. 2011, vol. 99, no. 8, p. 081901

[9] RINNERBAUER, V., EGELHAAF, H., HINGERL, K., ZIMMER, P., WERNER, S., WARMING, T., HOFFMANN, A., KOVALENKO, M., HEISS, W., HESSER, G., and SCHAFFLER, F. Energy transfer in close-packed PbS nanocrystal films. *Physical Review B*. 2008, vol. 77, no. 8, p. 085322

[10] USHAKOVA, E., LITVIN, A., PARFENOV, P., FEDOROV, A., ARTEMYEV, M., PRUDNIKAU, A., RUKHLENKO, I., and BARANOV, A. Anomalous size-dependent decay of low-energy luminescence from PbS quantum dots in colloidal solution. *ACS nano*. 2012, vol. 6, no. 10, pp. 8913–21.

[11] LITVIN, A., PARFENOV, P., USHAKOVA, E., FEDOROV, A., ARTEMYEV, M., PRUDNIKAU, A., GOLUBKOV, V., and BARANOV, A.. PbS Quantum Dots in a Porous Matrix: Optical Characterization. *J. Phys. Chem. C*. 2013, vol. 117, no. 23, pp. 12318–12324.

[12] PARFENOV, P., LITVIN, A., BARANOV, A., VENIAMINOV, A., and USHAKOVA, E. Calibration of the spectral sensitivity of instruments for the near infrared region. *Journal of Applied Spectroscopy*. 2011, vol. 78, no. 3, pp. 433–439

[13] PARFENOV, P., LITVIN, A., USHAKOVA, E., FEDOROV, A., BARANOV, A., and BERWICK, K.. Note: Near infrared spectral and transient measurements of PbS quantum dots luminescence. *The Review of scientific instruments*. 2013, vol. 84, no. 11, p. 116104

[14] PARFENOV, P., LITVIN, A., BARANOV, A., USHAKOVA, E., FEDOROV, A., PRUDNIKOV, A., and ARTEMYEV, M.. Measurement of the luminescence decay times of PbS quantum dots in the near-IR spectral range. *Optics and Spectroscopy*. 2012, vol. 112, no. 6, pp. 868–873

[15] LU, W., KAMIYA, I., ICHIDA, M., and ANDO, H.. Temperature dependence of electronic energy transfer in PbS quantum dot films. *Applied Physics Letters*. 2009, vol. 95, no. 8, p. 083102

[16] FOELL, Charles A, Keith A ABEL, Frank C. J. M. VAN VEGGEL and Jeff F. YOUNG. Kinetic analysis of the temperature dependence of PbSe colloidal quantum dot photoluminescence: Effects of synthesis process and oxygen exposure. *Physical Review B*. 2014, vol. 89, no. 4, p. 045139

[17] OLKHOVETS, A., HSU, R., LIPOVSKII, A.,and WISE, F. Size-Dependent Temperature Variation of the Energy Gap in Lead-Salt Quantum Dots. *Physical Review Letters*. 1998, vol. 81, no. 16, pp. 3539–3542.

[18] GAPONENKO, M., TOLSTIK, N., LUTICH, A., ONUSHCHENKO A., and YUMASHEV K.. Temperature-dependent photoluminescence Stokes shift in PbS quantum dots. *Physica E: Low-dimensional Systems and Nanostructures*. 2013, vol. 53, pp. 63–65

[19] RUKHLENKO, I., LEONOV, M., TURKOV, V., LITVIN, A., BAIMURATOV, A., BARANOV A.,and FEDOROV. A.. Kinetics of pulse-induced photoluminescence from a semiconductor quantum dot. *Optics express*. 2012, vol. 20, no. 25, pp. 27612–27635.

[20] LITVIN, A., PARFENOV, P., USHAKOVA, E., FEDOROV, A., ARTEMYEV, M., PRUDNIKAU, A., CHEREVKOV, S., RUKHLENKO, I., and BARANOV, A.. Size-dependent room-temperature luminescence decay from PbS quantum dots. In: *Proc. of SPIE*. 2012, p. 85641Z–85641Z–7