



The Picosecond Kinetic of Luminescence in Hydrophilic Colloidal CdS Quantum Dots

M.S. Smirnov^{1,*}, O.V. Ovchinnikov^{1,†}, A.G. Vitukhnovsky², S.A. Ambrozhevitch², A.V. Katsaba²,
 T.S. Shatskikh¹

¹ Voronezh state university, 1, Universitetskaya Pl., 394006 Voronezh, Russian Federation

² P.N. Lebedev Physical Institute of the Russian Academy of Sciences, 53, Leninskiy Pr., 119991 GSP-1, Moscow, Russian Federation

(Received 19 May 2013; published online 31 August 2013)

The picosecond kinetic of luminescence in conglomerations of hydrophilic colloidal CdS quantum dots with an average diameter of 2.5 nm in gelatin was investigated. It was observed in the recombination luminescence band with a maximum at 580 nm. A complicated character of depending in the time interval from 300 ps to 1800 ns was found. Obtained dependences were interpreted in terms of radiative recombination at the donor-acceptor pairs (different sizes), complicated non-radiative transitions involving localized charge carriers on deeper levels.

Keywords: Quantum dots, Auger recombination, Kinetics of luminescence decay, Donor-acceptor recombination.

PACS numbers: 72.20.Jv, 78.68.Hc, 61.72.uj

1. INTRODUCTION

Optical properties of colloidal quantum dots (QDs) are the basis for the development of one of the important areas of modern physics-nanophotonics. Practical interest in the photophysics of colloidal QDs and nanostructures with their participation is caused by a large range of practical applications for medicine, biology, optoelectronics and photocatalysis [1-6].

Processes of radiation and non-radiation degradation of electronic excitations in quantum dots play the important role in the formation of optical properties. The absorption and luminescence spectra provide information about the energy structure of QDs "bands", structural and impurity defects [7,8]. Non-radiative processes are multiphonon relaxation of electronic excitations on the levels of structural and impurity defects, localized mainly on the interface of colloidal QDs; non-radiative Auger recombination involving free charge carriers [9] and charge carriers, localized on the defects [10].

Photoluminescence properties are largely determined by the synthesis method of QDs [1]. It is high-temperature organometallic synthesis of colloidal QDs in a highly toxic solvent Trioctylphosphinoxide (TOPO). For this method there is predominantly "exciton" luminescence with a high quantum yield. The second method is to use sol-gel techniques in aqueous or aqueous ethanol mixtures in the presence of nontoxic polymer. These QDs have the luminescence associated with impurity-defect levels, and do not have the "exciton" luminescence.

This paper presents the results of a study of luminescence decay kinetics in colloidal CdS QDs in the gelatin in the time interval from 0.3 to 1800 ns. We tried to do model explanation of observed regulates. The currently known data about nature of luminescence centers and the picture of levels of structural and impurity defects in colloidal CdS QDs were considered.

2. INVESTIGATION METHODS AND SIMPLER

Investigation samples were colloidal CdS QDs, prepared by sol-gel method in an aqueous solution of gelatin. This method was described in detail in [11]. The preparing gelatin sol of colloidal CdS QDs was applied to a quartz plate of 2×2 cm² and dried.

The identification of colloidal CdS QDs was made using (TEM) LEO ~ 912AB ~ OMEGA transmission electron microscope with an accelerating voltage of 100 kV. Structural investigations were carried out by electron scattering method and the x-ray diffraction, using ARL X'TRA (Switzerland) diffractometer for K_{α1} copper. The absorption spectra of CdS QDs were obtained using Shimadzu BioSpec mini spectrometer (Japan). The luminescence spectra were investigated with help of Ocean Optics Maya ~ Pro 2000 spectrofluorometers. The luminescence decay kinetics was studied using PicoQuant TimeHarp ~ 100 TCSPC-system. QDs luminescence was excited by PicoQuant PDL 800-B pulsed diode laser (wavelength $\lambda = 405$ nm, duration of a pulse — 75 ps). The presented results were obtained at 300 K, 77 K and 10 K.

3. RESULT AND DISCUSSION

3.1 The Structural Properties of CdS QDs Samples

Fig. 1 inset 2 shows the distribution of CdS QDs in size, obtained by analysis of TEM images.

The average value of the diameter of CdS QDs was 2.5 nm. A half-width of the size distribution was < 35 %. Analysis of reverse electron scattering and X-ray diffraction (Fig. 1, inset 1) shows that the CdS QDs have a cubic lattice. Also the value of QDs size was obtained from half-width X-ray peaks using the Debye-Scherrer equation. It was shown that QDs have a size of a few nanometers.

* Smirnov_M_S@mail.ru

† Ovchinnikov_O_V@rambler.ru

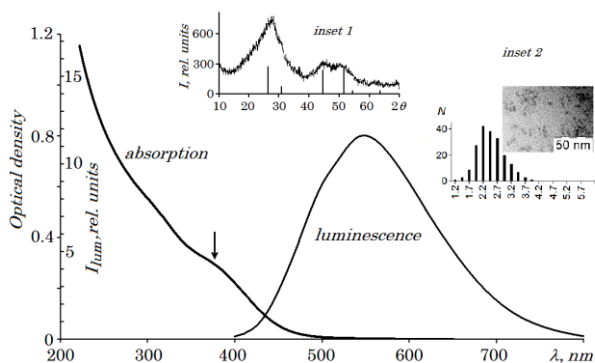


Fig. 1 – Absorption and luminescence spectra of CdS QDs ($d = 2.5$ nm). Inset 1 – X-ray diffraction image for CdS QDs, inset 2 – microscopic image and size distribution of CdS QDs

3.2 Luminescent Properties of CdS QDs Samples

For CdS QDs of average size (Fig. 1) we showed a broad absorption band with a special feature at 3.20 eV. This feature is the result of contribution to the absorption of the most probable "exciton" transition. For synthesized colloidal QDs the volume of effective band gap is much greater than the band gap of cubic single CdS crystal (2.42 eV).

A single broad band with a large Stokes shift (0.95 eV) of the luminescence band maximum relative to the exciton transition in absorption was a characteristic feature of observed CdS QDs luminescence (Fig. 1). At the same time, the absence of significant contribution of the exciton luminescence band in the resulting spectrum shows inhibition of this luminescence mechanism due to the rapid capture of photo carriers by defect-impurity traps.

Preliminary analysis of the size dependence of luminescence bands for CdS QDs in [7] and QDs synthesized by sol-gel technique in gelatin [11] showed that the maximum of the observed luminescence band is located between two bands of donor-acceptor recombination. These bands are characteristic for CdS. This comparison indicates that the observed photoluminescence band not elementary. And its appearance is the result of radiative recombination (D-A) pairs. According to [7] recombination is implemented with the participation of shallow electron (~ 0.1 eV) and deep hole traps.

The bands associated with band-impurity transitions (D-h and e-A) completely absent for available average size of QDs. In our case, it should be in the dark blue and blue-green spectrum regions.

Below we discuss the results of investigation of CdS QDs luminescence kinetics in the range 450-700 nm.

3.3 General Regularities of Luminescence Decay Kinetic in Colloidal CdS QDs

CdS QDs luminescence decay kinetic at 300 K is shown in Fig. 2. From the observed dependence we can do the following conclusions:

- The luminescence decay time for CdS QDs ($d = 2.5$ nm) for all investigated wavelengths is in the nanosecond range.
- The luminescence decay kinetic slows down as we move to longer wavelengths.
- These dependencies are not described by one or

two exponential functions. This indicates a complex pattern of recombination transitions in hydrophilic CdS QDs.

– There is a transformation of the luminescence spectrum of CdS QDs with the luminescence decay. There is long-wave shift of the maximum of the luminescence band with the luminescence decay. This shift reaches a value of 0.36 eV for the decay time of about 1000 ns.

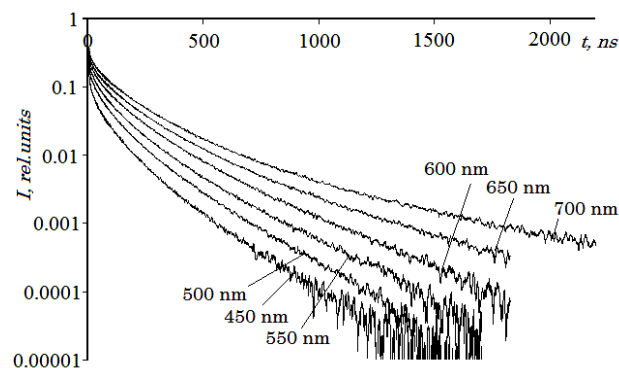


Fig. 2 – The luminescence decay kinetic in CdS QDs at 300 K

3.4 Temperature Dependence of the Picosecond Kinetic of Luminescence in CdS QDs

The luminescence spectra and luminescence decay kinetic of colloidal CdS QDs are noticeably changed when the temperature is decreased.

Changes in the luminescence spectra can be summarized as:

- The temperature decrease leads to a slight and non-monotonous change of position of the luminescence band maximum. At 80 K the maximum is shifted by 15 nm to longer wavelengths, and at 10 K it is shifted by 10 nm back.
- The luminescence quenching is observed when the temperature increase. It begins to manifest at 50 K. The luminescence intensity decreases by a factor of 3 at the temperature of 10-300 K.

The luminescence decay kinetic with decreasing temperature changes along the time scan range of 0.3 ns to 1800 ns. For normalized per unit of kinetics there are several features.

- Luminescence decay kinetics are complex. They can be described by superposition of 5 exponents.
- A view of the luminescence kinetic can clearly distinguish two regions. They are "fast" (at times up to 50 ns), and "slow" (at times more than 150 ns). The fast component has the greatest statistical weight for the short-wave part of the spectrum. With decreasing temperature, its contribution to the total kinetic picture is noticeably increased for all wavelengths, particularly for 450 nm and 500 nm (Fig. 2, 3).
- The statistical weight of the slow component with decreasing temperature (for times > 50 ns) decreases from 0.1 at 300 K to 0.01 at 77 K and to 0.001 at 10 K.
- For the slow component the time constant is aligned with decreasing temperature to 10 K in the case of luminescence kinetics, measured for all wavelengths (Fig. 3). The kinetics are parallel.

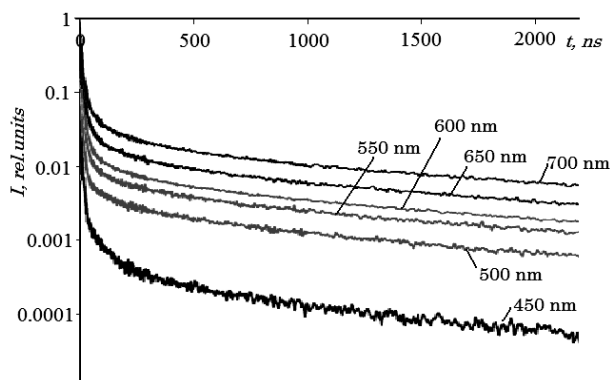


Fig. 3 – The luminescence decay kinetic in CdS QDs at 10 K

3.5 Discussion of observed kinetic regularities

The main feature was a slowdown of luminescence decay kinetic along the time scan range when we move to longer wavelengths. It leads to long-wave shift of the emission spectrum as damping. This regularity can have several reasons:

– *The recombination mechanism.* The center of recombination luminescence in QDs CdS, as noted in [8], is the donor-acceptor. This qualitative dependence is characteristic for such luminescence mechanism. It is due to the recombination of donor-acceptor pairs located at different distances from each other for variety quantum dots. As is known, the donor-acceptor nature of the emission allows us to estimate the energy of the Coulomb interaction between donor and acceptor in the pair.

$$\hbar\omega_{lum} = E_g - E_d - E_a + \frac{e^2}{\varepsilon|\vec{r}_d - \vec{r}_a|}, \quad (3.1)$$

where E_g is the band gap energy, E_d is the ionization energy of donor, E_a is the ionization energy of acceptor, $\hbar\omega_{lum}$ is the energy of emitted photon, e is the electron charge, $|\vec{r}_d - \vec{r}_a|$ is the distance between donor and acceptor, ε is permittivity.

For QDs of 2.5 nm, the Coulomb interaction energy was in the range from 0.30 eV (for distances donor - acceptor of 0.5 nm) to 0.06 eV (for a distance of 2.5 nm). Then, the maximum shift of the luminescence spectrum

can reach the value of 0.24 eV. It is of the order of magnitude as the observed changes. In addition, D-A pairs at different distances have different recombination time [12]. It leads to complex non-mono exponential dependence.

– *The size distribution of QDs in the conglomeration, which determines the position of the luminescence spectrum and its half-width.* The luminescence decay time for QDs of different sizes in the test conglomeration is different. It leads to a complication of the decay kinetic.

– *Interaction of QDs in the conglomeration during light absorption and transfer of electronic excitation energy from the luminescence centers of smaller QDs to the luminescence centers of larger QDs with the participation of several phonons* [13]. Despite the fact that the centers have the same structure. Then the luminescence kinetic at long wavelengths should be the slowest. We observe it in the experiment.

– *Non-radiative Auger recombination involving localized charge carriers.* If the excitation power of used semiconductor laser is 5 mW at 4×10^7 pulses/s, irradiation area of the sample is 4 mm², the absorption coefficient is 10⁴ cm⁻¹, then an electron-hole pair will be born in one of 10⁴ QDs. Then the probability of Auger process involving two excitons in a single QDs is negligible. On the other hand, as a result of Auger recombination the electron can transfer energy to electron, localized on acceptor. Luminescent centers will this acceptor.

– *The slow component of luminescence decay can be caused by the trapping of electrons into shallow traps.* They are not part of the luminescence center. Then for recombination electron must overcome the potential barrier. It will be accompanied by a slowing of the luminescence kinetic with lowering temperatures. The macroscopic local states due to a jump of the dielectric constant on «QD-matrix» boundary can be these shallow traps. Usually they are small with ionization energy less than 0.1 eV [14].

Apparently, in the case of hydrophilic CdS QDs in all of the above processes are implemented with some probably.

ACKNOWLEDGEMENTS

The work was supported by RFBR project №12-02-90827-mol-rf-nr and partially supported by RFBR project №12-02-31735-mol-a.

REFERENCES

1. D. Bera, L. Qian, T.-K. Tseng, P.H. Holloway. *Mater.* **3**, 2260 (2010).
2. P.T. Snee, R.C. Somers, G. Nair, J.P. Zimmer, M.G. Bawendi, D.G. Nocera. *J. Am. Chem. Soc.* **128**, 13320 (2006).
3. T. Pons, H. Mattoussi. *Ann. Biomed. Eng.* **37**, 1934 (2009).
4. P. Juzenas, W. Chen, Y.-P. Sun, M. Alvaro, N. Coelho, R. Generalov, N. Generalova, I.L. Christensen. *Adv. Drug Deliv. Rev.* **60**, 1600 (2008).
5. D.E. Prasuhn, A. Feltz, J.B. Blanco-Canosa, K. Susumu, M.H. Stewart, B.C. Mei, A.V. Yakovlev, Ch. Loukou, J. Mallet, M. Oheim, Ph.E. Dawson, I.L. Medintz. *ACS Nano.* **4**, 5487 (2010).
6. Y. Shirasaki, G.J. Supran, M.G. Bawendi, V. Bulović. *Nat. Photon.* **7**, 13 (2013).
7. A.I. Ekimov, I.A. Kudryavtsev, M.G. Ivanov, A.L. Efros, *J. Lumin.* **46**, 83 (1990).
8. J.R.L. Fernandez. *Surf. Sci.* **601**, 3805 (2007).
9. H. Htoon, J.A. Hollingsworth, R. Dickerson, V.I. Klimov. *Phys. Rev. Lett.* **91**, 227401 (2003).
10. Y. Kobayashi, T. Nishimura, H. Yamaguchi, N. Tamai. *J. Phys. Chem. Lett.* **2**, 1051 (2011).
11. O.V. Ovchinnikov, M.S. Smirnov, B.I. Shapiro, A.N. Latyshev, T.S. Shatskikh, E.E. Bordyuzha, S.A. Soldatenko. *Theor. Experm. Chem.* **48**, 48 (2012).
12. G.H. Döehler. *phys. status solidi b* **45**, 705 (1971).
13. O.B. Gusev, A.A. Prokofiev, O.A. Maslova, E.I. Terukov, I.N. Yassievich. *JETP Lett.* **93**, 147 (2011).
14. N.A. Efremov, S.I. Pokutniy, *phys. status solid* **27**, 48 (1985).